# REGIONAL EXTENSION CENTRE (C.L.R.I.) 220, Dharavi Road, Dharavi, BOMBAY 17, DD

# FANCY, SPLIT AND SPECIALTY LEATHERS

# **ACKNOWLEDGEMENT**

Grateful thanks are due to Shri T. S. K. Mahadevan, Scientist, who has helped us in Proof reading and corrections.

PRINTED AT
MANORAMA PRESS,
Madras-600 014.

# FOREWORD :

The book contains a series of very interesting articles on fancy, split and specialty leathers. These are by the scientists and technologists of the Central Leather Research Institute who have devoted all their lives to specialisation in the preparation of various types of finished leathers. In the context of the change in the complexion of leather trade and industry in India today when exports of finished leather and leather manufactures are insisted upon by the Government, a book of this type is not only timely and useful but most welcome to everybody connected with leather industry. The articles are very interesting in as much as minutest details are given with regard to preparation of various specialty leathers. I am hoping this book is a harbinger to a series of monographs on all aspects connected with the science, technology and engineering aspects of finished leather and leather manufactures which the Institute very hopefully contemplates to bring out in days to come.

The book makes very interesting reading and I am sure, the price is reasonable for the valuable information it presents in its pages. It is hoped that the book will be read widely by one and all.

January 31, 1975 Central Leather Research Institute MADRAS-600 020—INDIA

M. SANTAPPA

# INTRODUCTION

Today the production of fancy, split and specialty leathers has greater significance than ever. The industry is modernising itself in a serious effort to produce finished leathers. The task is no easy one and is beset with several problems. Among them are those of the profitable utilisation of splits and lower ranges of selection. Linings and fancy leathers are the normal outlets for such grades.

Splits and linings are the 'bread and butter' items of production in a tannery and their economic production and finishing can mean the difference between profit and loss. Fancy and specialty leathers finished out of the lower selections that normally go as linings can often prove lucrative to the tanner though for a temporary period only. The tanner has constantly got to strive for newer types in this area for the above reason.

Currently the nappa and softie leathers are in demand. Nappa from hides is an interesting item both for reasons of economy and 'cutting' value. The profitable utilisation of splits assumes greater importance in this context as hide nappa is split to 0.7 to 0.8 mm yielding a big area of flesh split.

Processes described in this booklet cover the varieties mentioned above. In addition, exotic items like reptile leathers etc., also receive coverage. Exotic leather dressing is on the wane because of ecological considerations. There is no reason, however, why there should not be a revival in this field. Farming of the species can be taken up on a big scale and these farms will provide the raw material without running counter to environmental principles.

Finishing of fancy leathers is an inexhaustible field. Antiquing, decalomania, tipping, finishing with foils, block-printing, screen-printing etc., are some of the possibilities and are adequately covered here. It is well to reiterate in this context that fancy finishing techniques should be so designed that the products finished still retain their natural feel and appearance and sheer away from producing a plastic look.

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J. C. DEB

In the West, sheepskins are generally used for making chamois leather. However sheepskins contain much grease and carry grease spots in the final leather. On the other hand, in India goatskins are considered quite suitable and satisfactory for producing chamois leather. The cheap rejection quality skins having hair-slip, scratches and such other damages on the grain side are usually selected for this purpose. The process practised elsewhere employ cod oil tannage. Cod oil is not available in India. So a formaldehydesardine oil combination tannage has been worked out and found suitable for making this type of leather. Whereas straight oil tannage necessitates splitting the skins in the beam house, this combination tannage makes possible removal of the grain layer by shaving or splitting, after formaldehyde retannage. Hence the present method can be practised even in small Indian tanneries which are equipped with shaving machine, drums and buffing machines only. The method is simple and produces quite satisfactory leather; the period of tanning too has been shortened.

# RAW MATERIALS

50 pieces of rejection quality wet salted Madras goatskins averaging 91-107 cm. (36-42") in size are taken.

# SOAKING

The skins are soaked in plain water in a paddle for 2-3 hours, taken out, broken over the beam on the flesh and washed thoroughly in running water ½-1 hour. The skins are then taken out, drained and weighed.

# **PAINTING**

Unhairing is done by painting a depilating paste made up of 1 part sodium sulphide and 15 parts slaked lime. Sodium sulphide is dissolved separately in hot water and then added to the mixture of lime and water. Care is taken to get a homogeneous paste and cool it to room temperature. It is better to prepare the paste two days prior to application.

The prepared paste is applied on the flesh side of the skin. The skins are then stacked on a platform flesh to flesh and left overnight in pile. Next day they are taken out, unhaired, put into a pit of old lime liquor (once used) containing 5% new lime on the soaked weight and left in this bath for two days. Hauling and replacing are done thrice a day.

#### RELIMING

Next day, the pelts are taken out, scudded and put into new lime liquor containing 10% slaked lime, 1% caustic soda and 300% water for two days in a paddle. The caustic soda is given in ½% doses both in the mornings and evenings for 2 days. On the third day, the pelts are examined for sufficient plumpness, taken out fleshed, scudded, weighed and washed thoroughly in running water for 15-20 minutes in a paddle.

# DELIMING

The washed pelts are then delimed with 1.0-1.5% boric acid or 0.5-0.75 ammonium chloride and 150-200% water (on the fleshed weight). The water and the stock are taken in the drum. Half the quantity of boric acid or ammonium in chloride is added and the drum run for 15 minutes. Then the other half is added and the drum run for another 45 minutes. The delimed pelts are scudded, washed, weighed and taken for tanning.

# TANNING

Formaldehyde pretannage: The delimed pelts are pretanned with 3.5-4.0% commercial formalin (40%), 0.75-11.00% soda ash and 175-200% water (on the delimed pelt weight). The pelts and water are entered into the drum which, is then started. The soda ash is dissolved separately and mixed with formaldehyde in a bucket of water. The formaldehyde solution is then fed into the rotating drum through the hollow axle in three instalments at intervals of 30 minutes. The drumming is continued for 4-5 hours to complete the formaldehyde tannage at pH 8.5. The skins are then horsed up overnight. Formaldehyde tanning can also be done as follows. The skins are drummed with 100% water and ½-1% acetic acid given in two feeds at 15 minutes' interval for 1 hour till the pH of the cut section is 5-5.5. The bath is drained and 3% conc. formalin is added dry to the goods and the drum is run for 1-2 hours. 100% water is then added and 1% soda ash is added in slow feeds to the bath and the drum is run for 1 hour. The pH of cut section should be 9.0-9.5. The pieces are piled overnight. Next morning they are

sammed and the grain layer is removed with the splitting machine. (This can be done with shaving machine also). They are then shaved on both sides uniformly. The shaved weight is recorded and the skins are kept overnight in cold water. Next morning, the water is squeezed out and the skins are ready for oil tanning.

Tanning with sardine oil: The shaved skins are then tanned with 18-25% sardine oil (Iodine value 135-170 and acid value 15-30) 0.50-0.75% soda ash, 7-8% calcium carbonate and 7-8% water (on the shaved weight). The sardine oil is first mixed with calcium carbonate in a wooden vat. The soda ash is separately dissolved in water and added to the oil mixture to be made into an emulsion whose pH is adjusted to 7.5. The skins are now smeared with this emulsion by dipping and care is taken to spread it uniformly on both the sides. The pieces are now put into the drum. The drum is then run for 6 hours and the skins are left in it. Next morning the drum is run for another 4-6 hours until the chamoising smell is noticed. The skins are then taken out and hung up in the air for oxidation for 7-10 days during which period they turn mustard yellow in colour. Now the goods are ready for washing.

#### DEGREASING

The oxidised skins are then weighed and degreased with 3.5-4.0% soda ash and 0.5-1.0% detergent Noigen LS (Chika Ltd.) or Sandozine NI (Sandoz India Ltd.) or Corilene DG (ICI) on the oxidised weight. The oxidised skins are first soaked in a drum with sufficient quantity of water and half the quantity of detergent at 45-50°C. The drum is then run for ½ hour and drained. The skins are washed three times with 1/3rd quantity of soda ash given above for ½ hour each time at 45-50°C, using a fresh float of warm water each time. Finally the skins are washed for ½ hour with the remaining quantity of detergent at the same temperature. They are then again washed in luke-warm water, taken out and hung up for drying in air.

# STAKING

The dried skins are then staked with considerable pressure. The skins should be of cream colour and absolutely nongreasy.

# BUFFING. TRIMMING AND MEASURING

The staked skins are then buffed on a buffing machine with 180 grit emery paper on both the sides. Finally they are buffed on the flesh side only with 320 grit emery paper or on a buffing wheel. The skins are then trimmed, measured and assorted.

# CHAMOIS LEATHER BY FORMALDEHYDE, SULPHOCHLORINATED OH AND SARDINE FISH OIL COMBINATION TANNAGE

# J. C. DEB, E. R. SARGUNAR & Y. NAYUDAMMA

In this process, sulphochlorinated mineral oil produced on pilot plant scale at CLRI, Madras is used. This oil in combination with a small quantity of sardine fish oil produces a very satisfactory leather. The process is found useful where a pale cream coloured product is desired and also when it is difficult to obtain regular supplies of fish oil.

# PROCESS DETAILS

The raw materials and other process details are exactly the same as for the method described already for the manufacture of chamois leather by formaldehyde-sardine oil combination tannage (vide pp. 9-11). Only the oil composition used for tanning is different i.e., 10-12% sulphochlorinated oil, 3-5% sardine fish oil, 0.5-0.75% soda ash, 7-8% calcium carbonate and 7-8% water (on the shaved weight) are used in the oil composition.

The physical test data of the finished leathers produced by the experimental process and the normal method are given below.

t	Shrin emper (°C	ature	Break streng (1b	th.	te	ation st ecs)	Sinking test (in secs	abs	Water orption ost**
	Parallel	Perpendi cular	Parallel	Perpendi cular	For Gaselin*	Fo Water*	In dividual values	Average	84
Control lot.							30		
with 20% sardine fish oil	72	72	140	<b>79</b> <sub>.</sub>	35	305	12 15	19	301
Expt. No. 1 with — 12% sulphachiorinated oil, 5% fish oil in goatskins	76	77	131	90	57	313	75 50 60	62	310-6
Expt. No. 2 with—12% sulphochlorinated oil, 5% fish oil in sheepskins	75	74	75	70	20	315	40 3.5 30	35	338.2

<sup>\*</sup> According to Federal standard specifications. \*\* According to Indian standard specifications.

Parallel and perpendicular indicate the directions of sampling with reference to the backbone line.

# CHROME CRUST AND MORDANTED CRUST FROM WET SALTED GOAT SKINS

# J. C. DEB, K. VENKATARAMAN, P. S. VENKATACHALAM & Y. NAYUDAMMA

Today there is considerable interest in importing crust and mordanted crust goat skins by the Western dressers in view of the following advantages. The freight charges will be considerably less as crust leathers will weigh 40-50% less than wet blue leathers. No dispute or misunderstanding is likely to occur between buyer and seller as there will be practically no difference between the 'crust' area and finished leather area whereas the difference can be enatically wide where wet blue and finished leathers are compared.

The main drawback in the case of crust leathers is the difficulty experienced by the dresser in wetting it back to its original state and dyeing it uniformly and brightly. Even if the leather can be successfully wetted, a raised and broken grain results when the leather is finished. This difficulty has not yet been overcome but today in view of the shortage of leather, the finisher has no difficulty in selling such leathers and has therefore no objection to imparting crust as such a measure will greatly reduce his effluent problems in addition to gaining the other advantages already listed. Besides a prominent grain is in fashion today as it enhances the natural look of leather. In view of the growing demand and developing market for chrome crust leathers and in response to a number of enquiries received from the industry, a suitable process for the manufacture of chrome crust and mordanted crust has been worked out as detailed below.

#### RAW MATERIALS

50 pieces of wet salted Frode quality goatskins averaging 81-86 cm. (32-34") in size are taken.

#### SOAKING

The skins are paddle-soaked in plain water to remove the salt; the paddle is run for 1-2 hours. They are then taken out, trimmed, broken over the beam with a blunt knife and paddled in fresh water for one hour. The skins are taken out, drained and weighed (soaked weight).

# LINING (by flooding method)

The Minhairing is effected through a depilating paste composed of 1 part sodium sulphide and 15 parts slaked lime. Sodium sulphide is dissolved separately in water and then added to the mixture of Minhe and water. Care is taken to get a homogeneous paste which is amonoised to room temperature. It is better to prepare the paste one day prior to its application on the skins.

The paste is applied on the flesh side. The skins are then piled up in a pit flesh to flesh. The pit is flooded with water so that the piles are kept just immersed in water. The goods are left undisturbed for 5 days. On the 6th day, the skins are taken out, unhaired and put into new lime liquor containing 2.0-3.0% slaked lime (on the soaked weight) in a paddle for one day. Next day, they are examined for sufficient plumpness, taken out, fleshed, scudded and weighed (ueshed weight). The pelts are washed thoroughly in a paddle for 1/2 hour.

# DELINING

The skins are delined in a bath consisting of 0.5-0.75% ammonium sulphate and 100% water (on the fleshed weight), in a drum for 30 minutes. On testing a cut section with phenolphthalcin, the midthird portion alone will react red indicating the presence of alkali i.e., the pelts are two-third delimed. They are then washed and bated.

# BATING

Overnight bating method is followed.

The washed skins are bated in a covered paddle using 1.0-1.5% Oropon (Rohm) or any other proprietory goat skin bate (on the fleshed weight). The bath is made up with half the quantity of bate using one paddleful of water (300% water at normal temperature) and the skins are paddled for one hour. Next, 2 oz. sodium flouride per 100 gallon of liquor (i.e., 8 g. per litre) dissolved in one pint (600 ml.) of water at 40°C is added to the bath and the paddle is run for 5 minutes. The pelts are left in the bath overnight.

Next morning, the remaining half of the bate is added and the temperature of the bath is raised to 38-40°C by passing steam. The pelts are paddled in the bath maintaining the temperature of the bath at 38-40°C until the goods are satisfactorily bated. The pH of the bate liquor before unloading should be 7.8-8.0; if not, it should be adjusted to that pH.

After the completion of bating, the pelts are taken out, scudded well, washed in cold water and put to the pickling process.

# **PICKLING**

The pelts are pickled overnight in a drum using 6% common salt, 100% sulphuric acid, formic acid and 75-100% water (on the fleshed weight). Salt is first dissolved in water formic acid is next added and the skins are drummed in this bath for 5 minutes. Sulphuric acid is then diluted and added to the revolving drum through the hollow axle and the pelts are drummed for one hour and left in the pickle bath overnight.

Next morning, the pelts are drummed for  $\frac{1}{2}$ -1 hour and the pH is adjusted to 3.0-32. After pickling, the pelts are taken out and the bath is drained. They are now ready for chrome tanning.

### TANNING

Tanning is done in a drum by the one both chrome tanning process.

Chrome extract powder (B & C Mills) may be used for chrome tanning. The power contains 25%  $Cr_2O_3$  and the chrome liquor prepared by dissolving one part of the powder in 3 parts of hot water and left overnight will have a basicity of 33 1/3% and a pH value of about 3. Half the volume of the liquor is made 50% basic by adding 90 g. of soda ash to 1.0 kg. of chrome extract H. powder. This liquor is kept separately.

2% salt and 75% water are taken in a drum which is started. The pickled goods are put in and the drum is run for 5-10 minutes. The chrome liquor (33% basic equivalent to 0.8% (n.O.) is now added and the drum which is run for 30 minutes. The second instalment consisting of the balance of 33% basic liquor and an equal quantity of 50% basic liquor (total 9% Cr.O.) is then added and the drum run for 45 minutes. The third instalment (50% basic; 0.8% Cr.O.) is then added and the drum run for 2 hours. Then the bath is, basified using a mixture of 2% Hypo, ½% soda bicarb, and 1% sod, formate given in 3 feeds at intervals of 16 minutes. The drum is run for one more hour. The pH of the leathers should be temperature will be 105-108°C. The skins 3.6-4.0. Shrinkage are then washed in the diluted chrome bath for 5-10 minutes and piled overnight.

The goods are then sammed, shaved uniformly and the shaved weight is noted. The shaved leathers are well soaked back, washed in two changes of water and neutralised with 0.5% sodium bicarbonate 0.5% sodium formate and 300% water (on the shaved weight) for 1 hour and then washed in two changes of water. (PH of cut section after neutralisation should be 4.00-4.50). They are now ready for the subsequent operations. The succeeding operation depends on whether chrome crust or mordanted crust is required.

For chrome crust leathers, the neutralised pieces are dry-drummed with 0.25-0.5% Neowet, an anionic wetting agent or Noigen L x 100 or LT 180 which are nonionics (Chika Ltd.), and 0.5% polyethylene glycol (NOCIL) for 30 minutes. 1.2% calsolene oil HS \*ICI) is also added and the drum is run again for 15 minutes. The skins are then horsed up.

# MORDANTED CRUST

For mordanted crust leathers the neutralised goods are treated with 3% raisonene oil HS (ICI) and 100% water at 50°C for 30 minutes. Then 2% mimosa extract + 2% Basyntan DLE dissolved in a small quantity of water are added and the drum run for 30 minutes. The goods are then taken out and horsed up.

Next day, the goods (chrome crust as well as mordanted crust) are put in the putting out machine, oiled up with 2 parts kid finishing oil and 1 part fish oil, sammed, set out by machine and hung up for complete daying for two days. Then they are kept in pile for 2-3 days.

# STAKING AND BUFFING

The dried goods are now saw-dusted, staked lightly by a staking machine. They are then buffed on the flesh side, trimmed and assorted.

The crust leathers so obtained could be dyed and finished into a wide variety of leathers that could ordinarily be obtained from wet or dry salted goatskins.

Note: It may however be noted that each tanner has his own specific methods of tanning and finishing depending upon the end use and the requirements of the customer. The Indian exporter may do well to first ascertain from the foreign buyer as regards his requirements of chrome, oil, vegetable tan and wetting agent that may be incorporated in the chrome crust.

# REWEITABLE DRY BLUE CHROME AND COMBINATION TANNED CRUST LEATHER

# K. T. SARKAR AND S. N. GUPTA

It is recognised by the tanners that sorting in the crust stage is far more reliable than sorting in the wet blue stage. Accordingly, instead of carrying out retanning/dyeing and fatliquoring straightaway after chrome tanning, it is sometimes convenient to keep chrome tanned stock in the crust form for several weeks so that it can be carefully sorted for finished leathers which are the best selling and the most fathionable in the season.

Once dried chrome leather proves extremely difficult to wet back in the normal way. Many "wetting out agents" have been tried but abandoned because dried chrome leather could not be wetted back both easily and economically.

For the last two years CLRI has been giving its attention to this question. CLRI has found out that certain chemical treatments of the freshly chrome tanned goods, prior to drying, facilitate easy and economical wetting back later. The procedure is simple. The "wetting out chemicals" are added either in the last phase of chrome tanning process or in a separate bath after tanning and washing, and give satisfactory results on almost all types of tannages namely full chrome, chrome-aluminium, chrome-zirconium, chrome formaldehyde, chrome-syntan etc. The chemicals added are the following:

- (i) Neutral polyhydroxy compounds containing ether group or polyether compounds containing hydroxyl groups.
- (ii) Esters of polyglycols and dicarboxylic acids namely succinic, maleic, fumaric, phthalic acid and their sulpho products.

Since fully chrome tanned leathers in the wet stage are exported in large quantities, greater attention has been given to rewettability of straight chrome tanned leathers; however, combination tannages of chrome with syntan, aldehyde, zirconium, sulphochlorides etc., would give better rewettable properties.

The following working recipes are recommended to the tanneries interested in the export of dried blue chrome or chrome combination tanned leather (chrome being the predominant tanning agent) with readily wettable characteristics:

	(Ch	emicals based on pelt weight)
(i)	Noigen EL 40 (Dai Ichi Karkaria Ltd. Polyethylene glycol 600 (Nocil)	0.3 — 1.5% 0.4 — 1.0%
(ii)	Noigen LRW (Dai Ichi Karkaria Ltd. Glycol	2.0 — 2.5% 0.4 — 1.0%
(iii)	Ammonium oleate Isopropyl alcohol (Nocil) Diethylene glycol (Nocil)	2% 1.5% 1%
(iv)	Noigen I.T 180 (Dai Ichi Karkaria Ltd. Oxitol (Shell Chemicals)	0.5 — 2.0% 0.5 — 0.8%
(v)	Noigen LT 180 (Dai Ichi Karkaria) Noigen LP (in case of hides only) Polyethylene glycol 600	0.5 - 1.0% $0.2 - 0.5%$ $1.5 - 2.5%$
(vi)	Ammonium oleate Polyethylene glycol 600 Liq. ammonia to adjust pH to 6.2 — 6. Noigen LP P	1.0 - 2.0% $1.5 - 2.0%$ $0.3%$

The percentages are based on the weight of the leather and the compactness of the fibre structure. The quantities of the chemicals should be determined according to substance, nature and age of tanned leather, fat content and the degree of tannage. The treated leathers are piled, struck out and act as usually practised. Finally, they are booked to dry out.

#### THE WEITING BACK PROCESS

The process of wetting back is much the same as is followed in the case of vegetable tanned crust, namely (a) stripping, souring, splitting/shaving, washing and the retanning/dyeing/fathquoring as desired.

# STRIPPING (chemicals based on crust weight)

The crust leathers are dipped for about 1-2 hours in 500% water at 50°C, and then washed in warm water for 20-30 minutes.

# SOURING

Drum for 5 minutes with 100% water and 2% salt. Then add 0.5% acetic and 0.2-0.4% sulphuric acid, drum for 45-60 minutes, drain and wash for 20 minutes. Split and shave to required substance. The subsequent processes may be carried out as desired.

# J. C. Deb, K. Venkataraman, P. S. Venkatachalam & Y. 'Nayudamma

Processes for the manufacture of book-binding and chamois leathers from gostikin splits are presented here. The method involves splitting the pelt in the lined condition and utilising the skiver for the manufacture of book-binding leather, hat straps, wallet leather etc. and the flesh split for chamois leather. Skins having a backbone length of over 90 cm. (36") are quite suitable for this purpose. Bigsized goatskins available in different parts of India will constitute an ideal raw material for this work. From the economic point of view, the products would work out to be cheap as two types of leathers are made out of one raw material. This is a regular practice in other countries utilising Australian and New Zealand sheep skins as the raw material. This interesting field may be profitably exploited by Indian tanners. The finished products are satisfactory in quality and strength.

# RAW MATERIALS

50 pieces wet salted Madras quality goatskins of average size greater than 90 cm. (38") are taken.

#### SOAKING

The selected goatskins are trimmed and soaked in a paddle in plain water for 1-2 hours. They are then taken out, broken on the flesh side over the beam and washed thoroughly in fresh water for 1-2 hours in the running paddle; next they are horsed up to drain and weighed (soaked weight).

# UNHAIRING AND LIMING

The unhairing is done with a depilating paste made up of 1 part sodium sulphate and 15 parts, slaked lime. Sodium sulphide is dissolved separately in hot water and the sulphide solution is then added to the mixture of lime and water. Care is taken to get a homogeneous paste which is then cooled down to room temperature. [It is better to prepare the paste one or two days prior to application.]

The paste is applied on the flesh side of the skins which are then stacked on a platform flesh to flesh and left in pile overnight. Next day, they are taken out, unhaired and put into 300% once used old lime liquor and 5% slaked lime (on the soaked weight) and left overnight in the pit, handling being done twice a day.

#### RELIMING

Next day, the pelts are taken out, scuided and put into fresh lime liquor containing 10% slaked lime and 300% water and left overnight in the pit hauling and replacing being done thrice a day. Next day, another 5% slaked lime and 0.5% soda ash are added, hauling and replacing are again done thrice a day. On the third day, 0.5% soda ash is added and hauling and replacing are done thrice during the day. The pelts are left overnight in the pit. On the fourth day, they are fleshed by machine and put into the same lime liquor and left for 2 hours after strengthening the bath with 5% slaked lime. Then the pelts are taken out and replaced after strength the liquor with 0.5% soda ash. The goods are handled for 10-15 minutes and left overnight.

Next day, the skins are washed and split into two halves, the grain splits being taken for the manufacture of book-bindig skivers and the flesh splits for the manufacture of chamois leather. The weights of the skivers and flesh splits are noted (pelt weight).

# A. BOOK-BINDING SKIVERS FROM THE GRAIN SPLITS

50 pieces skivers: pelt weight — 31.8 kg. (70 lb.).

# WASHING

The skivers are washed thoroughly in plain water in a drum.

# DELIMING

Deliming is done with 1% sodium bisulphite, 0.5% acetic arid and 100% water (on the pelt weight). 100% water and the washed pelts are taken in a drum. 1% bisulphite is then added and the drum run for 15 minutes. 0.5% acetic acid dissolved in a small quantity of water is added into the revolving drum through the hollow axle and the drum run for 30 minutes. The goods are then taken out, scudded, washed and pickled.

# **PICKLING**

The delimed pelts are then pickled with 10% salt, 1% sulphuric acid and 100% water (on the pelt weight). Salt is first dissolved in water in a drum and the goods are entered into it and run for 5 minutes. Sulphuric acid is then diluted and added into the revolving drum through the hollow axle in two equal instalments at an interval of 10-15 minutes. After the last addition, the drum is run for one hour and the goods are left in the bath overnight. Next day, the drum is run for ½ hour and the goods are taken out for chrome tanning. The pH of the exhaust bath would be about 2.8.

# CHROME TANNING

6% B & C chrome extract powder (corresponding to 3% bichromate of soda) is dissolved in 10% water and used for chrome tanning. (The pH of the liquor would be about 3). Molasses reduced chrome liquor of 33% basicity also may be used for tanning.

3% salt and 100% water (on the pelt weight) are taken in a drum and the pickled goods are put in and the drum is run for 5-10 minutes. The dissolved chrome liquor is added in two instalments. The first instalment of the liquor is added to the drum which is run for 30 minutes. The second instalment is added and the drum run for 2 hours more. The goods are then basified with 0.5% sodium bicarbonate dissolved in a little water and added in two feeds at an interval of 15 minutes. Drumming is carried out for one more hour. The goods are then removed and horsed up overnight (pH after basification would be 3.5).

After chrome tanning, the skivers are samned, weighed and divided into two lots containing 25 pieces in each lot and retanned as described hereunder.

#### FIRST LOT

25 pieces skivers: pelt weight — 12.3 kg. (27 lb.).

# WASHING AND NEUTRALISATION

The tanned skins are washed in two changes of water. The goods are neutralised with 0.5% sodium bicarbonate and 100% water (on the samned weight) in a drum for 30 minutes. This is followed by thorough washing and retaining.

# RETANNING

Retanning is done with 4% Tanigan Supra DLE (BASF) or CLRI SYNTAN PC and 100% water (on the shaved weight). The neutralised goods and water are taken in a drum which is set in motion. The dissolved syntan is then added into the revolving drum in three feeds at 10 minutes' intervals. The drum is run for  $1\frac{1}{2}$  hours more. The goods are then washed and fatliquored.

# **FATLIOUORING**

Fatliquoring is done in two separate baths.

First fatliquoring: The retanned skivers are now fatliquored in a drum with 0.75% CLRI FATBASE F, 0.75% TRO., and 100% water (on the shaved weight). Water at 50°C is taken in a drum. The stock is entered into the drum and the drum started. The fatliquor made into an emulsion is added into the revolving drum through the hollow axle and the drum run for 30-45 minutes. The goods are then horsed up and are now ready for second fatliquoring.

Second fatliquoring: The second fatliquoring is done in a separate bath with 1.0% catron liquor O (BASF) and 100% water (on the shaved weight). Water at 50°C is taken in a drum. The goods are entered into the drum and run. The fatliquor in the form of an emulsion is added into the revolving drum through the hollow axle and the drumming is continued for 20 minutes. The skivers are then piled up on a horse overnight.

# SECOND LOT

25 pieces skivers: shaved weight — 11.3 kg. (25 lb.)

# WASHING AND NEUTRALISATION

The goods are washed in two changes of water and neutralised as described earlier.

#### RETANNING

The goods are retained with 8% myrob extract powder, 0.5% formic acid and 100% water (on the shaved weight). The neutralised skivers and water are taken in a drum which is set in motion. The dissolved myrob extract is then added in one feed and the drum run for one hour. The pieces are then taken out and washed with water for ½ hour. Fatliquoring is done as described earlier.

# SAMMING, OILING UP, SETTING AND DRYING

Next day, the leathers of both the lots are struck out in the putting out machine. A mixture of two parts foots-free fish oil and one part kid finishing oil is applied on the grain side and the leathers are hung up in the shed for sammying. The sammed leathers are set out and hung up for complete drying.

# SAW-DUSTING, NAILING AND TRIMMING

The dried leathers are then saw-dusted overnight in moist saw-dust to condition them for staking. The conditioned leathers are then staked in a Slocomb staking machine and nailed on wooden board and dried. Next day, the skivers are taken out, trimmed and finished

#### FINISHING

The leathers are finished into black as follows:

Stain coat: Stain coat is prepared with 25 g. methic leather black, 25 g. acetic acid, 72 ml. 10% lineeed mucilage and water to make 48 kg. The skivers are first stained with stain coat on the grain side by a brush and then dried.

Bottom coat: Bottom season coat consists of 180 g. GLRI black pigment paste, 45 g. nigrosine, 45 g. hematine, 15 ml. ammonia, 180 g. 10% casein solution, 100 g. of Binder SH (Handymens) 10 g. T.R.O. and water to make 3.6 kg. One pad coat of this season is applied on the grain side and allowed to dry. Now 240 ml. 40% formaldehyde is added per 4.8 kg of the bottom season and a second pad coat of the same is given on the grain side. After drying, the leathers are staked and cold plated with light pressure. One spray coat of the same season is then applied and allowed to dry.

Top fixing coat: Top coat is prepared with 1 part 10% casein solution, 1 part neutral formaldehyde (40%) and 4 parts water. The skivers are given a spray coat and allowed to dry. They are then glazed, measured and printed into morocco grain. They may be assorted if desired.

# B. CHAMOIS LEATHER FROM THE FLESH SPLITS

50 pieces flesh splits: pelt weight — 48.8 kg. (90 lb.).

#### WASHING'

The fleshed splits are washed thoroughly in running water for 15-20 minutes.

#### DELIMING

The washed pelts are then delimed with 0.5% ammonium chloride and 100 water (on the pelt weight). Deliming is carried out in a drum  $\frac{1}{2}$  hour. The pelts are then scudded, washed, weighed and taken for tanning.

### **TANNING**

The delimed pelts are pretanned with 3.5-4.0% formaldehyde 0.75-1.0% soda ash and 175-200% water (on the pelt weight). The pelts and water are entered into the drum which is then started. The soda ash is dissolved separately and mixed with formaldehyde in a bucket of water. The formaldehyde solution is then fed into the rotating drum through the hollow axle in three instalments at intervals of 30 minutes. The drumming is continued for 4-5 hours for completion of the formaldehyde tannage (pH 8.5). The pieces are piled for 2 hours and then hooked overnight for sammying. Formaldehyde tanning can also be done by the alternative method described earlier. Next morning, they are shaved on both sides uniformly and weighed (shaved weight). The splits are kept in cold water for a few minutes, then squeezed out and taken for oil tanning.

The shaved splits are then tanned with 20-25% sardine fish oil, 1.0-1.5% soda ash and 8-10% calcium carbonate (on the shaved weight). Sardine oil is first mixed with calcium carbonate in a wooden vat. Soda ash is separately dissolved in water and worked into the oil mixture to yield an emulsion; the pH is adjusted to 9.5. The emulsion is applied on both sides uniformly and the splits are drummed for 4 hours and rested overnight. Next morning, the drum is run for another 4-5 hours until a chamoising smell is noticed. The splits are then taken out and hung up for oxidation for 7-10 days during which period the pieces turn mustard yellow in colour. They are now ready for degreasing.

# DEGREASING

The oxidised stock is weighed and washed as follows:

1st washing: The goods are drummed with 800% cold water (on the oxidised weight) for 30-45 minutes and drained.

2nd washing: The above procedure is repeated using hot water (45°C) instead of cold water.

3rd washing: This wash is given with 200% tepial water (45°C) and 0.5% Noigen LS (Chika Ltd.) for 30-45 minutes. The splits are removed and drained.

4th washing: The goods are washed with 200% tepial water (45°C) and 2% soda ash for 30-45 minutes and drained.

5th & 6th washings: The soda ash wash is repeated.

7th washing: The goods are washed again with 200% tepial water (45°C) and 1.5% Noigen LS for 30-45 minutes.

# OIL TANNING

Last washing: Washing is done with 800% hot water (45°C) for 30 minutes. The pieces are then rinsed in cold water, squeezed and hung up for complete drying.

# **STAKING**

The dried chamois pieces are then staked using a Slocomb staking machine. The skins should be of cream colour and absolutely nongreasy.

# BUFFING, TRIMMING AND MEASURING

The staked leathers are now buffed on a buffing machine with 180 grit emery paper on both sides. Finally, they are buffed on the flesh side only with 320 grit emery paper or on a buffing wheel. They are then trimmed, measured and assorted.

# BOOK BINDING LEATHERS BY ALUM AND MYROBALAN COMBINATION TANNAGE

# M. S. OLIVANNAN & R. SELVARANGAN

The book-binding leathers must be durable and strong. The principal characteristics of this type of leather are pleasing feel, appearance, toughness and durability. Usually the leathers are tanned with pyrogallol type of tannin. In Western countries pure sumac tanned or sumac retanned leathers containing certain buffer salts like Citrate or tartrate are preferred. In India we have got enough myrobalan (a pyrogallol type of tannin) for the tanning. But it does not produce full and durable leathers as such. Modification of myrobalan tannins has been carried out by many workers. But still it is not being used as a single tanning material. Hence a systematic study on the utilisation of myrobalan for book-binding leathers was undertaken at the Central Leather Research Institute and the process developed is given below:

# RAW MATERIAL

Wet salted goat skins are used.

# SOAKING

The goat skins are trimmed and soaked in a paddle for three hours in plain water. They are taken out, worked over a beam and then washed again in a paddle for 30 minutes with fresh water. They are hauled up, drained and then weighed. The soaking operation may be suitably altered for dry and dry salted goods.

# LIME PAINTING

The skins are painted on the flesh side with the following: 2% sodium sulphide (on the soaked weight) 10% slaked lime ( —do— )

The sodium sulphide is dissolved in minimum amount of hot water and cooled. The solutions of sodium sulphide and the lime are mixed together with enough water to make a homogenous paste. The paste is applied uniformly on the flesh side, and the skins are paired flesh to flesh and then piled. The piled skins are covered with a gunny.

#### LIMING

Next day the skins are unhaired and put into the prepared lime liquor made up of

10% slaked lime 150% old lime liquor 150% fresh water

The unhaired skins are handled thrice and immersed in the liquor. On the second day of liming the skins are handled thrice; on the third day 0.5% caustic soda previously prepared and cooled is added to the lime bath and the skins are handled thrice. On the fourth day of liming the skins are hauled up, fleshed in a fleshing machine, scudded over a beam and washed thoroughly in a drum for 30 minutes. The fleshed weight is noted.

# DELIMING

The washed skins are delimed with 1% ammonium chloride (on the fleshed weight) and 150% water. Complete deliming is done in a drum for one hour and checked with phenolphthalein. The defimed skins are scudded over a beam and washed thoroughly in a drum for 30 minutes. Now the skins are ready for myrobalan tanning.

#### MYROBALAN TANNING

(i) pH adjustment and then tanning.

The delimed and washed skins are transferred to a wooden tube containing 2% salt; and 150% water. The skins are handled in this for 10 minutes. Then the pH of the bath is carefully adjusted to 4.5 using requisite amount of diluted hydrochloric acid in the course of two hours. The pH adjusted pelts are housed to drain and are ready for myrobalan tanning.

Myrobalan liquor (10° Barkometer) is prepared using solid myrobalan extract. The float may be maintained between 200% to 400% on the fleshed weight. It is required here that the skins must be well immersed inside the tan liquor and at no time the skin should come out of the liquor. This may lead to bad staining on the surface of the skins. The pH of the myrobalan bath is adjusted to 4.5 using soda ash solution. Now the skins are repeatedly handled in this till a uniform colour is obtained and then immersed in the bath. Throughout the tanning the pH is maintained at 14.5. In this way the skins are kept in 10° Bkr. liquor for three days and 15° Bkr, liquor for four days. Each day the barkometer and the pH.

are readjusted. On the last day the skins are removed from the tub; rinsed with water and worked over a beam. They are then oiled with 4% raw ground nut oil by hand. The oiled skins are hooked up till they become semictry. Next day the sammed skins are set well by hand (or by machine) and immediately taken for aluminium tanning.

(ii) Buffer treatment and then tanning: (all materials on the fleshed weight).

The pelts are drummed with the following:

Borax	1%
Sodium bisulphite	1%
Oxalic acid	 0.5%
Water	100%

The pelts are taken in the drum containing 100% water. Borax and sodium bisulphite are dissolved together and then added to the drum. The drum is run for five minutes. Now the oxalic acid is added in the form of a solution and the drum is run for 10 minutes.

The myrobalan tanning is done as follows: 20% myrobalan spray dried extract is dissolved in warm water (100% water at 60°C) and then cooled to room temperature. The tan liquor is added to the buffer treated pelts in three instalments. First instalment of the liquor is added to the drum which is run for 45 minutes. The second instalment is then added and the drum is run for one hour. The third instalment is then added and the drum is run for three hours. The Tanning must be done in a vegetable tanning drum. The drum speed must be slow and it may be stopped at frequent intervals in order to dissipate the heat evolved during the course of the drumming. If the pH of the exhaust bath is above 4.5 the pH of the bath may be brought to 4.2 to 4.5 using 0.5% oxalic acid in the form of solution.

The skins are removed from the drum, rinsed in running water and then horsed to drain. They are then beamed over a beam or set in a machine and oiled by hand with 4% groundnut oil. The oiled skins are hooked to dry.

Next morning when the skins are in sammed condition, they are set by hand or in a machine and taken for aluminium retanning while still in the wer condition.

# ALUMINIUM RETAINING.

- (a) Preparation of basic aluminium sulphate liquor:
  - (i) Aluminium sulphate (iron free) 1 kg. (Al<sub>2</sub>(SO4)<sub>3</sub> 18 H<sub>2</sub>O Lixiviate Water (hot/boiling) 1 lit

Leave for one hour

- (ii) Add with stirring Sodium citrate 70 gms. till it is completely dissolved.
- (iii) With continuous stirring, add soda ash. 350 g. dissolved in 2 litres of water in the course of about an hour till all frothing ceases.
- (iv) Make up the stock solution to 30% aluminium sulphate (i.e., 30 g) aluminium sulphate/100 c.c. of water). This has a basically of 66% and pH 3.8-4.0).
- (b) Aluminium tanning (all weights are based on fleshed wt.)
  Aluminium sulphate (66% basic) ... 6.6%
  Formaldehyde ... 0.5%
  Water ... 100.0%

The skins are taken along with 100% water in a drum and run for 10 minutes. Then the basic aluminium sulphate liquor is added in two instalments at an interval of 30 minutes. Then the formaldehyde is added and the drum is run in all for 3 hours. Now the pH of the bath is checked. If it is below 4.2, the pH of the bath is raised to 4.2 using about 1% sodium bicarbonate. The bicarbonate is dissolved in twenty times of its own weight and added in several instalments. Frequent checking of the bath pH is essential as otherwise the aluminium sulphate precipitates instantaneously.

The tanned skins are then taken out. They are then washed in a drum for five minutes and then horsed to drain. The drained skins are fatliquored with the following:

Turkey red oil	•••	1%
Borax	•••	0.5%
Groundnut oil	***	2%
Water at 50°C	•••	100%

The skins are taken along with warm water in a drum. The emulsified oil is then added to the drum through the hollow axle. The drum is then run for 30 minutes and then horsed.

Samming, Setting and Drying: Next day the leathers are struck out in the putting out machine and hung up for samming. The sammed leathers are set out in a setting machine and hung up for complete drying.

Sawdusting, Nailing and Trimming: The dried leathers are then saw-dusted overnight in moist saw dust to condition them for staking. The conditioned leathers are then staked in a staking machine and nailed on wooden boards and left overnight. Next day the skins are trimmed, buffed on the flesh side and finished.

A general process for book-binding leather is given above. Since the tanned leathers are thick and plump, they may be split in a splitting machine to a required thickness when they are still in wet condition. They are then levelled in a shaving machine. Care must be taken to avoid iron staining. It is better to adopt lime splitting which is considered to be advantageous in many respects including avoidance of iron staining and better utilisation of flesh splits.

#### FINISHING

(i) Brush dyeing and aniline finish (Golden brown colour):

Bottom coat: The skins are given one brush coat with 5% muclage solution and aired off. The skins are then plated and a stain coat is applied.

Stain coat: Stain coat is prepared with 5 g. Metanil yellow (ICI), 5 g. Naphthalene orange (ICI), 60 ml. 10% casein solution and water to make 1000 ml. The skins are then given a uniform brush coat and aired off.

Top coat: Top coat consists 60 g. egg albumin, 60 ml. milk, 120 ml. 10% casein solution, 60 ml. formaldehyde and water to make 1000 ml. The skins are given one pad coat, aired-off, plated and then sprayed to cover. They are then glazed.

# (ii) Glazing lacquer finish:

# Staining:

Suitable basic dye	7 gms.		
Acetic acid	•••	7 ,,	
10% linseed mucilage	•••	50 ,,	
Water to make	•••	1000 ml.	

The above staining is given one brush coat and aired-off.

The skins are then sprayed with 1 part CLRI lacquer (suitable colour) and 2 parts Spartan thinner (Addison Paints & Chemicals). The skins are sprayed liberally with this lacquer and aged for one day. Then they are glazed.

# (iii) Pigment finishing:

Staining is given as for (ii).

# Season coat:

150 gms.
200 ,,
100 ,,
100 ,,
16 ,, ) mix together
16 ,, mix together 4 ,, and then add
10 ml.
1500 ml.

The skins are given one brush coat and aired off. They are ironed and given another brush coat. Then they are glazed and given one spray coat to cover after adding 30 ml. of formaldehyde per litte of the season.

# Top coat:

Neran glaze.	50 gms.
Ox blood	100 ,,
Binder SH (Handymans)	50 ,,
Water	500 ml.

The skins are sprayed well and aired-off.

# Fixing coat:

Formaldehyde	1.	•••	1 part.
Water			3 parts.

The skins are given one liberal coat of fixing and aired off. The dried skins are glazed and smooth plated.

(iv) Resin finish: The skins may also be finished using synthetic resin emulsion.

The skins are padded on the grain side with a 5% solution of linseed mucilage, dried and then cold plated. They are then brushed with the following and dried.

Suitable pigment paste	•••	1	part
Synthetic resin emulsion		1	part
10% casein solution		14	part
10% wax emulsion		10	part
Water	•••	2 to 3	parts

To the above season 30 ml. formaldehyde per litre is added and then sprayed to cover uniformly.

# Fixing coat:

5%	casein	solution	•••	1 part
10%	neutr	al formaldehyde	•••	1 part

The fixing coat is sprayed liberally and dried. The dried skins are hot plated and assorted.

W. N. PANDAV

Raw dried goat skins imported from Africa are generally full of defects and possess a coarse and open grain. Hence they are employed in making cheap lining leathers for the local footwear trade. These skins are, of late, finding a wider use because of the high cost of Indian goat skins now being exported either as E.I. tanned or finished leathers or pickled or blue-chrome stock. The process detailed below has been developed to produce leathers suitable for making wallets, purses and similar leather goods.

### RAW MATERIALS

Suspension or air dried goat skins of East African origin are used. Best results are obtained when goods are assorted in 3 sizes (large, medium, small) and processed in separate lots.

# SOAKING

1st day: Dried skins of a particular size are weighed and soaked in drum. (About 45-50 kg. of dried skins weigh 100 kg. after soaking). The soak bath is made up in a drum using 600% water (on dried weight), 0.1% sodium sulphide and 0.1% Idet (Swastik Oil Mills, Bombay) on volume basis. The skins are entered into the drum, plunged well and left still in the bath overnight.

2nd day: The drum is run for about 30 minutes. The skins are subsequently drummed for 5 minutes every hour for 4 hours. The soak water is then drained and the goods are dry-drummed for one hour. Fresh water is then added and the drum run for 30 minutes. The skins are taken out and put in the paddle for liming. (Alternatively, soaking may be done either in a paddle or a pit).

# LIMING

The paddle containing 250% once used lime liquor, made up with 250% of fresh water, is started and the skins are entered one by one. The paddle is then run for 10 minutes and the goods are left there overnight.

3rd day: 3% sodium sulphide previously dissolved in water is added to the running paddle and the paddle is run for 10 minutes every hour for 4 hours. 7% lime is then added and the skins are left overnight.

4th day: The paddle is run for 30 minutes both in the morning and evening with intermediate runs of 5 minutes every hour.

# RELIMING AND FLESHING

5th day: The goods are hauled out and relimed with 500% water and 10% lime. The paddle is run for 10 minutes per working hour.

6th day: The paddle is run for 10 minutes per working hour after making an addition of 0.25% caustic soda to the bath in the morning.

7th day: The goods are fleshed and weighed. The lime liquor in the paddle is made up with about an equal quantity of water and used for liming the next pack.

#### DELIMING

The stock is delimed with 100% water and 1% ammonium chloride. The drum is run for 15 minutes and the goods are left still in the bath overnight.

8th day: The drum is run for 10 minutes and the bath drained.

# BATING

The stock is bated for one hour using 150% water (37°C) and 1% Bate powder (Lechinol & Co. Ltd., Calcutta). The goods are hand-scudded and washed in 250% water for 20 minutes. The bath is then drained.

### PICKLING

Pickling is done with 6% salt, 1% sulphuric acid and 80% water. Sulphuric acid diluted with 10% water is added slowly to the drum after the pelts are run in brine solution for 15 minutes. Goods are drummed for one hour and left overnight.

9th day: Drum is run for 15 minutes. The pH of the cut section is checked and found to be 2.5.

# CHROME TANNING

1% bichromate equivalent chrome liquor is added to the drum in one instalment and the drum run for 2 hours. The bath is basified with sodium bicarbonate to a pH of 3.8. The goods are horsed up.

10th day: The leathers are sammed and shaved to even thickness. The shaved weight is recorded and the goods are kept dipped in water overnight.

11th day: The shaved stock is washed in cold water for 30 minutes and the bath is then drained.

# RETANNING

The skins are retained with 1.25% Tanigan CH (Bayer India Ltd.) and 35% water for 30 minutes. 25% spray dried Mimosa extract is added to the drum which is run for 25 minutes each hour for 2-3 hours. During this time, tanning is completed. The goods are now piled overnight.

# **FATLIQUORING**

12th day: The leathers are washed in drum using 100% cold water for 10 minutes. 1% Sorbolene S.T. (Castrol Ltd.), 1% T.R.O., 0.75% castor oil, 0.75% karanja oil and 1% Saginal T. liquid (on weight of the oil) are mixed well and added to the bath. The drum is run for 30 minutes. Then 4% myrobalan extract powder is added and the stock again drummed for 30 minutes. The skins are rinsed momentarily in water and piled.

13th day: The skins are set out on the machine and oiled with 2% pongam oil.

# SAMMYING, SETTING AND STAKING

The skins are hung for sammying, set out twice and stored in crust stage. They are then assorted for various shades, lightly staked, buffed with 100 grit paper on flesh and snuffed with 240 grit paper.

#### FINISHING

Dye wash: 1 oz. basic dye of suitable shade and 1 oz. acetic acid are made up to a gallon.

Pigment coat: 12-16 oz. pigment paste, 10 oz. casein solution and 2 oz. T.RO. are made up to a gallon. Two brush coats and one spray coat are given. The goods are glazed.

Top coat: 10% more pigment paste is incorporated in the bottom coat and the season is mixed well and a good coverage of the grain obtained.

Fixing coat: I part neutralised formaldehyde diluted with 4 parts water is added to 1 part 10% casein and the mixture used for fixing the season. One coat is sprayed and the leathers, when dry, are plated or ironed. The goods are now glazed.

#### RESIN FINISHING

The leathers with grain defects are snuffed on the grain. One pad coat of the following season is given: 100 parts pigment paste, 100 parts Acryl Binder M.S. (CLRI), 25 parts casein 10% solution, 10 parts 10% wax emulsion and 500 parts water. The same season is sprayed to obtain good coverage of the grain.

Top spray: 1 part Spartan clear lacquer (Addison Paints & Chemicals, Madras) is mixed with 3 parts Spartan thinner.

A light spray coat is given and the leathers are plated at 120°F.

# K. Parthasarathy, K. T. Sarkar, P. Sambasiva Rao, & Y. Murali Manohar

Recently there has been an increase in the overseas demand for cow hide nappa leathers. These leathers are mainly used for making fancy leathergoods with a "softie touch" (or a 'buttery-feel' as they call it) for footwear, furniture upholstery, garment etc. The availability of good quality cow hides in India is limited and hence Indian tanners are at a disadvantageous position in supplying the bulk requirement of nappa leathers currently in demand in the overseas market. However, a search for a suitable alternative raw material revealed that Indian buffalo calf could produce on equally attractive nappa leather having a soft and mellow touch approaching that of glove and garment. Moreover, buffalo calf has a peculiar grain pattern which makes it more appealing.

In order to manufacture successful nappa leather the tanners should strive for the following objectives:

- (a) The grain should be fine and should have the best possible break.
- (b) The leather should have an extremely soft "handle" with good grain elasticity.
- (c) An increase in the fullness and roundness of the finished leather maintaining the rubber-like bounce of a chrometanned leather.

To manufacture this type of leather, the main concern of the tanners should naturally be from the stage of retanning but it must be pointed out that for quality nappa leathers, the process begins earlier i.e., they are influenced by all operations before and after retanning.

A series of experiments were conducted in the tannery division of the Central Leather Research Institute. Two processes which were found to give the most satisfactory results are described here.

# NAPPA LEATHERS FROM BUFF CALF SKINS

## RAW MATERIAL

Wet salted buffalo calf skins.

Weight range 3-4 kg. average, free from grain defects.

#### SOAKING

500% water

0.2% Sodium trichlorophenate

0.2% Tinovetin NR (Suhrid Geigy Ltd.)
(Overnight)

## LIMING

300% Water

0.2% Noigen LS (Dai-Ichi)

3.5% Sodium sulphide Flakes (Travancore Chemicals).

4.0% Lime (slaked).

2.0% Common salt.

Handling is done twice a day.

Duration-20-22 hours

Next day, the hides are unhaired, fleshed and relimed.

## RELIMING

300% Water.

4.0% Slaked lime.

3.0% Common salt.

Handling is done twice a day

Duration-20-22 hours.

Next day, the hides are refleshed, scudded and weighed. (pelt weight is noted).

## DELIMING

200% Water

1.2% Ammonium chloride.

0.8% Sodium bisulphite.

Period of drumming 40-60 minutes.

Complete deliming is done. Colourless to phenolphthalein Washed for 10 minutes in 300% water.

## **PICKLING**

10% Water

2% Salt

Drumming time—10 minutes

+ 0.5% Formic acid

0.7% Sulphuric acid

0.3% Formaldehyde

10% Water

The above mixture is added at a time to the drum. Then the following is added in one feed immediately after adding the above mixture.

10% Chrome extract

10% Water

0.6% Calcium carbonate

0.6% Sodium acetate

0.3% Soda ash

Then the drum is run for 2 hours. pH 3.0. Then the following is added:

50% Water

0.4% Sodium sulphite

0.5% Soda ash added at a time

Drumming period—1 hour. pH 3.8-4.0. Piled overnight. Next day, the leathers are sammed and split to 1.0 mm.

The shaved weight is noted. Then the pieces are retanned with 8% CLRI Chrome Syntan complex for 1 hour with 50% float. Piled overnight.

Next day, the leathers are washed for 10 minutes in 300% water.

## **NEUTRALISATION**

200% Water

0.5% Sodium formate

+ 0.5% Sodium sulphite

1.0% Soda bicarb

10% Water

Period of drumming — 45 minutes. pH 5.0-5.50. The leathers are washed for 10 minutes in 300% water.

## DYEING

200% Water 50°C.

0.7% Atul Direct Black (Atul Products Ltd.)

0.2% Chlorazol Dark Green PLS (I.C.I.)

+ 0.2% Derma Carbon GTS (Sandoz India Ltd.)
Drumming period — 20 minutes.

+ 2.0% Wattle Extract Solid

Drumming period — 30 minutes.

+ 5% Sandozol KBS (Sandoz India I.td.)

2% Sulphited fish oil

5% Sulphated neatsfoot oil

Drumming period — 1 hour.

+ 0.3% Formic acid

3% Water

Drumming period — 20 minutes and piled overnight.

Next day, the leathers are set out, conditioned, reset and toggled to dry. Then saw-dusted, staked, trimmed, buffed on flesh side.

## **FINISHING**

## BLACK

Basic Black (ICF)			2 g.
Malachite green			0.25 g.
Acetic acid			3 cc.
Water		•••	1800 cc.
Eukesol oil ground	(BASF, India)	•••	200 g.

The above mixture is applied on the grain side by pad. Dried overnight. Next day, the leathers are polished on the grain side in the buffing machine by reversing the buffing paper.

## SEASON

Hilco black pigment 51	(Handyman)	
	,	(paste)
Derma carbon GTS		10 g.
15% Hard casein binder	•••	10 g.
10% Wax emulsion		. 20 g.
Water	, •••	. 650 cc.
Binder PA 110 (Chika L	td.)	150 g

Two full cross coats are sprayed to give light coverage.

#### TOP COAT

EMG Lacquer (BASF India Ltd.) ... 1 part
Water ... 0.5 part
Slip Agent (Polyacrylamide) ... 0.05 part

Applied by spray, dried and milled for 2 hours.

## NAPPA LEATHER FROM COW HIDES.

## RAW MATERIAL

Wet salted cow hides averaging 10 kg. per piece.

#### SOAKING

The hides are soaked overnight.

500% Water

0.2% Noigen LP (Dai Ichi)

0.2% Sodium trichlorophenate

Next day, the hides are given two changes of water.

## LIMING

Painting

2% Sodium sulphide

1.5% Slaked lime

4.5% China clay

25% Water

The hides are dipped in the above sodium sulphide mixture and piled for 5 hours. Afterwards, the hides are relimed.

## RELIMING

400% Water

4% Sodium sulphide

4% Lime (slaked)

0.2% Noigen LS (Dai Ichi)

The hides are kept in the above reliming bath for 12 hours with one or two handlings. Next, the sides are washed for 5 minutes in drum with 400% water and then split to 1.8-2.00 mm. Then, they are scudded and the pelt weight is noted. They are now washed for 10 minutes and delimed.

#### DELIMING

400% Water

1.0% CLRI Picktan N

1.0% Ammonium sulphate

The drum is run for 45 minutes till the hides are completely delimed. Then, they are washed for 10 minutes in 400% water.

#### PICKLING

10% Water

2% Salt

Period of drumming — 10 minutes.

## Then added .

0.7% Sulphuric acid

0.5% Formic acid

0.3% Formaldehyde

20% Water

Then immediately added the following:

10% Chrome extract (Golden Chemicals)

0.6% Sodium acetate

0.6% Calcium carbonate

0.3% Soda ash

The above chemicals are added as such in powder form and the drum is run for 2½ hours. Then added the following:

50% Warm water

The drum run for 2½ hours; the pH was 3.6-3.8; piled overnight. Next day, the leathers are sammed, split to 1.3 and then shaved to 1.1 mm. thickness. The shaved weight is noted.

The shaved leathers are washed for 10 minutes in plain water of 400%.

#### RECHROMING

40% Water

5% Chrome Extract Powder (Golden Chemicals)

5% Water to dissolve chrome extract

2% Cation liquor '0' (BASF, India)

The drum is run for 10 minutes.

Then added to the same bath:

3% Formaldehyde

2% Sodium acetate

in 3 instalments

at 15 minutes' interval.

Then the goods are drummed for 40 minutes.

Then added the following mixture in 4 instalments at 10 minutes' interval:

1.0% Sodium formate 0.5% Sodium sulphite 0.5% Soda bicarb 15% Water

After the last feed of the above mixture, the drum is run for 30 minutes, pH-5.0-5.5; piled overnight.

#### NEUTRALISATION

The leathers are washed in 400% water for 10 minutes; drained.

100% Water 0.5% Basyntan FC (BASF, India)

The drum is run for 30 minutes; then the leathers are washed for 10 minutes in 400% (float).

## **FATLIQUORING**

4% Lipoderm Liquor 2 (BASF, India) 0.5% CLRI cationic fatliquor TW

The drum is run for 1 hour; piled overnight. Next day, they are set in the machine and dried; then, the sides are wetted back with:

800% Water
1.5% Liquor ammonia
1.5% Tinovetin NR (Suhrid Geigy Ltd.)

The drum is run for 30 minutes. The goods are then washed for 20 minutes in 400% water at 50°C.

## **DYEING**

500% Water ... 50°C

1% Basyntan M ... (BASF, India)

The drum run for 10 minutes.

Add 1-2% suitable dye, run 30 min.

Added to the same bath:

2.5% Lipoderm Liquor 2

1.0% Cationic fatliquor TW (CLRI)

The drum run for 40 minutes.

## Added:

1% Formic acid

10% Water

Given in 3 feeds at 5 minutes' intervals; then added 3% Irgalan SFC (Suhrid Geigy). The drum run for 30 minutes.

Then the leathers are piled overnight. Next day, set and dried, then saw-dusted, staked, toggled, trimmed, buffed and finished.

## **FINISHING**

15 g. Hilco organic Blue Pigment (Handyman)

5 Hilco white 101 Pigment (Handyman)

300 g. Binder B 41 (Indofil Ltd.)

400 g. Water.

10 g. T.R.O.

25 g. 10% Wax emulsion

Two full cross coats are sprayed. Then, they are hair-cell plated and again sprayed with one more coat of the above season and dried.

## TOP COAT

100 g. E.M.G. Lacquer

50 g. Water

One to two cross coats sprayed; the leathers are dried and milled in drum for 2 hours. They are then removed, brushed and assorted.

# GRAIN GARMENT LEATHERS FROM RAW SHEEP SKINS

# T. S. K. Mahadevan, T. S. Krishnan, A. Ganesan & P. S. Venkatachalam

In the Punjab area, there has been growing interest in the manufacture of grain garment leather for winter-wear. The garment leathers made at present are from vegetable tanned leathers which are neither strong nor are finished in fast colours. The process described here aims at the manufacture of a chrome tanned grain garment leather at a reasonable cost with indigenous materials.

## **RAW MATERIALS**

Thin spready wet salted sheep skins 0.557 sq. m. (6 sq. ft.) without any grain damage are used.

## SOAKING

The skins are given a thorough soaking in two changes of water for about 3 hours. They are drained and weighed.

#### LIMING

The skins are given a fairly long liming so as to effect a good opening up of the fibres. The soaked stock is put in an old lime liquor containing 10% lime (about 35% available CaO content) and 3% sodium sulphide of 50% purity (on the soaked weight). They are kept in this bath for 7 days with periodical handling. The pelts are then unhaired, fleshed and relimed for about 2 days with 5% lime and 300% water (on the soaked weight). They are then taken out, weighed and delimed.

#### DELIMING

Deliming is done in a drum using about 0.5% ammonium sulphate with 250% float of water (on the pelt weight). After deliming, the skins are scudded, washed in cold water for ½ hour, then given a warm water wash for 10 minutes and taken for bating.

Note: All the processes are carried out in wooden vats to suit the convenience of the small tanner.

#### BATING

I.5% Pancreol 3AS and Pancreol 5AS (in equal parts) and 300% water at 35°C (on the delimed pelt weight) are mixed well and the stock is handled in this bath for 10 minutes and left overnight. Next day, the skins are shifted to a warm water bath 35°C and handled for 3-4 hours. Then the adhering flesh is scraped off and the skins are scudded.

## **PICKLING**

Pickle liquor is prepared with 2% sulphuric acid (Sp. gr. 1.74), 8% salt and 200% water (on the delimed pelt weight). The skins are handled in a tub containing the pickle bath and left overnight, taking care to spread the skins within the bath. Next day, the skins are taken out, checked for completion of pickling using bromophenol blue indicator and then piled over a wooden horse, the skins being spread flat and tight. The skins are kept piled for 3 days. Each day, a small quantity of the pickle liquor is poured over the skins to avoid their drying up. Then, the sammed and drained weight of the skins in the pickled stage is noted.

#### DEGREASING

The grease and fat in the skins are removed using 12.5% kerosene (on the sammed weight) and 1.00-1.25% Noigen LP (Chika Ltd.), on the weight of kerosene. The skins are dipped one by one in this mixture, kept for 15 minutes and the excess kerosene is squeezed out by hand; the fat comes out as a whitish emulsion. This operation is repeated thrice more. Since the bath would become very greasy, it is changed and another bath is made up as mentioned before. The skins are dipped in this one by one, the fat is squeezed out by hand and then the skins are left overnight in the same bath so as to remove the last traces of fat.

Next day, the skins are taken out and the excess fat is squeezed out by beaming. Now the skins are degreased (the bath is greasy).

- Note: (i) If not much grease is coming out in the second degreasing bath (as most of the fat is likely to be removed in the first bath itself), the quantity of kerosene used in the second degreasing bath can be reduced to half the quantity mentioned.
  - (ii) Also degreasing can be done in a drum, when the lot is bigger, using about 12.5-20.0% kerosene depending upon the fat content of the stock. The

mixture and the stock can be put in the drum which is run for \(\frac{2}{4}\)-1 hour; most of the fat will be removed by this time.

## BRINE WASHING

The skins are trampled in a 10% solution of common salt in water for  $\frac{1}{2}$  hour. This is repeated 3-4 times gradually reducing the salt concentration in the succeeding baths and finally ending the washing in plain water. At this stage the wash water should be clear.

## PREPARATION OF CHROME LIQUOR

Chrome liquor is prepared with 5% commercial sodium dichromate, 4.5-5.25% sulphuric acid (Sp. gr. 1.74), 4% saw-dust (local safeda, bodhulu saw-dust as available in Kashmir) and 15% hot water at 40°C (on the pelt weight).

The dichromate, water and acid are mixed together and the moist saw-dust is added slowly. The mixture is stirred. After all the saw-dust has been added, it is kept overnight to allow the reaction to be completed.

Note: The saw-dust reduced liquor thus prepared is found to give a very light whitish leather.

Next day, the liquor is tested for completion of reduction. The chrome liquor thus prepared is kept for one day before use. It is filtered through gunny cloth before using the same.

## CHROME TANNING

A bath is prepared with 6% common salt and 300% water in a tub. Half the quantity of chrome liquor is first fed in and mixed well. The degreased skins are put in and trampled for one hour; the second half of the chrome liquor is now added and the skins are handled for ½ hour and then piled grain to grain over a horse, tightly stretched. Next day, the skins are again dipped in the chrome liquor, handled for 30 minutes and piled stretching well over a horse. In the afternoon, they are checked for completion of penetration. The 1% sodium bicarbonate is added and mixed well; the skins are handled and the pH of the bath is kept at 3.5. Then the skins are put back, handled for ½ hour and are then taken out and piled over a horse. Next day, 0.25% soda bicarbonate is added and the

skins are handled for 4 hours. (pH of the bath kept at 3.7). In the evening, they are taken out and piled. Next day, another 0.25% soda bicarbonate is added (pH about 3.8). The skins are handled for 4 hours, taken out and piled over a horse, after carrying out the boiling test.

Note: Chrome tanning can also be done in a drum using 10% B & C basic chrome extract. The salt bath used can be the same as mentioned earlier. In this case, the chrome tanning and basification upto a pH of 3.8 can be done over a period of 3 hours. After chrome tanning, the skins are taken out and piled over a horse.

The chrome tanned skins are kept piled over a horse for a day. Then they are taken from the pile, sammed and worked on the flesh side over a beam so as to remove any loose tissue on the adipose layer. Alternatively, the skins can be shaved on a shaving machine to level the substance. The shaved weight is noted.

The shaved skins are washed in 500% cold water for 10 minutes in a tub. Then the water is changed and 1% soda bicarbonate dissolved in 500% float is added. The skins are left overnight in the same bath. Next day, the completion of neutralisation is tested using bromocresol purple. The cross section should be blue.

The neutralised skins are put in a drum with 600% float of cold water; the drum is run for 10 minutes. Then the skins are washed in warm water (40°C) for 10 minutes, drained and dyed.

#### DYEING

The skins are dyed with 2% Dermalight Brown GRL (Sandoz India Ltd.) and 250% hot water at 45°C (on the shaved weight). The skins are first put in hot water; the drum is run for 2 minutes. The dye is dissolved separately in hot water (6 times the weight of dye) and the pH of this dye solution adjusted to 7 using ammonia. Then this dye solution is added to the drum in two instalments at 10 minutes interval. The drum is now run for 20 minutes. A small piece is cut from a skin and it is ensured that the dye has penetrated through more than half the thickness of the skins.

#### **FATLIOUORING**

The fatliquor is prepared with 10% B.O.C. leather oil (Burmah Shell Co.) and 50% hot water on the shaved weight). The oil is Fancy—6

emulsified in hot water and the pH of the same is adjusted to 7.5 using acetic acid (since the pH of the emulsion is initially above 10). Then the same is added in two instalments to the dye bath itself at 10 minutes interval. After the second addition, the drum is run for ½ hour. By this time, the dye has almost completely penetrated. Then 0.25% acetic acid diluted four times is added and the drum run for 10 minutes.

## RETANNING

4% myrobalan extract powder is dissolved in 3 times its weight of water and the pH of the same is adjusted to 4.5 using soda bicarbonate. This is added in one feed into the drum and run for 45 minutes. The retanned skins are taken out and piled over a horse.

# REFATLIQUORING AND OILING

In the sammed state, they are oiled off on the grain with a mixture of 1% gingelly (til) oil, 0.5% glycerine, 0.5% soft tallow and 0.5% kerosene (on the shaved weight) as a very thin light coat and allowed to dry slowly, the skins being put in an open room. Then they are conditioned in saw-dust and given a light staking. Then in order to effect a dry drumming action, the skins are beaten over a wooden horse for  $\frac{1}{2}$  hour, or the skins can be dry drummed for 2 hours for better effect. They are again given a good staking and shaved lightly on the flesh side; a good buffing can be done. The skins are now taken for finishing.

## **FINISHING**

The skins are cleared on the grain side with a 0.1% solution of Noigen LS (Chika Ltd.).

They are aired off and sprayed with the following coloured season to obtain coverage.

Dermalight Brown GRL (Sandoz India	Ltd.)	0.5 g.
Dark Brown Pigment (Handyman)		16 g.
Black Pigment (Handyman)	•••	12 g.
Primal S1 (Rohm & Haas)	•••	20 g.
Primal B41 (Indofil Ltd.)	•••	20 g.
B.O.C. Oil	•••	45
Wax Emulsion	•••	10 g.
and Water to make	•••	100 cc.

The leathers are polished with cloth to produce a smooth feel.

# The pieces are now sprayed with a protective coat:

EMG Lacquer (BASF)	100 parts
Catalix GS (Sandoz India Ltd.)	5 parts
Water	50 parts

They are now aired off and polished with cloth. If a brighter face is desired, the protective coat is again sprayed and this is followed by a spray coat of thinner.

# WHITE CHROME

## SHEEP LINING LEATHERS BY TANNING IN VATS

# (Laie) K. RAJABATHER, M. MUSTAFA & P. S. VENKATACHALAM

This process for vat tanning of white chrome sheep lining leathers has been specially worked out keeping in view the needs and limitations of the village tanner who is not in a position to use machines or other equipment like drums, etc., for his operations. The choice of chemicals and other materials is again limited to those that are within his easy reach.

The alum tanning technique for white sheep skins is not unknown to the cottage tanner, but with the advent of readymade chrome extracts in the market, he has shown interest in producing a chrome tanned lining leather with a white surface, as this is becoming increasingly popular for shoes as well as for sandals. The present method aims at an alum-chrome-alum combination tanning in view of the tanners' familiarity with alum pretanning. Such a combination produces softer leather with a less prominent backbone and free from the damp feel usually associated with leathers tanned solely with alum. Use of imported syntans has been avoided. Neither drums nor machines are employed for this process.

## RAW MATERIALS

25 wet salted sheep skins weighing 41 kg. (90 lb.) are used.

#### SOAKING

The skins are soaked for about an hour (flesh side up) in plain water and cut open. Then they are washed thrice, thorough trampling being given between each change of water. They are piled to drain for about ½ hour and weighed.

#### UNHAIRING

A lime-sulphide paint is prepared using 12% lime paste, 1.5% sodium sulphide and sufficient water (on the soaked weight) to yield a syrupy paste. This paste is applied on the flesh side of each skin after which each skin is folded along the backbone line and piled

flesh to flesh overnight. The skins are unhaired and relimed with once used second lime liquor reinforced with 12% lime paste and sufficient water to cover the goods. The skins are handled twice during this period. Next day, they are scudded and again limed in a bath consisting of 400% water, 12% lime paste and 0.125% caustic soda. The skins are handled twice and left overnight in the same bath. The next day, they are handled thrice. The following day, the goods are fleshed by hand and weighed. They are then scudded, washed thrice and fleshed. The sequence of operations is repeated and the pelts are now left in plain water overnight.

The next day, the skins are delimed with 0.25% ammonium chloride and 0.2% oxalic acid and sufficient water to cover goods.

## PICKLING

After the completion of deliming the cut section is found to be neutral to phenolphthalein; the skins are scudded, washed, drained and pickled with 15% common salt, 1.5% formic acid and 150% water (on the pelt weight).

Note: In case formic acid is not found suitable for reasons of economy, a mixture of 1.0-1.5% sulphuric acid and 0.5% acetic acid may also be used, though this will not produce the same bright white leather as in the other case.

The skins are trampled in the pickle bath for about ½ hour and then left overnight in the same bath. Next day, 0.5% formic acid or 0.25% sulphuric acid is again added and the goods are trampled for about ½ hour and left overnight in the same bath. On the following day, the skins are piled grain to grain on a wooden horse and aged for a period of 3 days.

## TANNING

3% alum is added to the original pickle bath. The stock is entered into this bath and handled for about ½ hour. 1.5-2.0% B & C chrome crystals previously dissolved in sufficient quantity of water is now given approximately in six equal instalments at intervals of 30 minutes. The skins are then left overnight in this solution. After handling the goods for some time the next day, 3% alum is added and the handling continued. After 3-4 hours, 1.5-2.0% soda bicarbonate dissolved in sufficient quantity of water is added slowly with constant stirring. After handling for a further period of ½ hour,

the skins are left in the same bath overnight. Next day, the shrinkage temperature is found to be 95°C. The skins are piled to drain and weighed the next day.

The weighed goods are then washed six times using plain water. After washing, the pH of the cut section of leather should be 4.0-4.5. Then they are fatliquored for ½ hour with 4% T.R.O., 1% raw coconut oil, 5% french chalk and 100% hot water at 45°C (on the tanned and drained weight).

After the absorption of the fatliquor, the skins are piled grain to grain on a wooden horse and left overnight.

Next day, a thick paste of kaolin and a little soap is applied uniformly on both sides of the skins which are then hooked to samm. When they are in sammed condition, the skins are staked by hand and again hooked. This is repeated twice before the skins dry out completely. Finally they are fluffed on the flesh side, staked again, trimmed lightly and measured.

S. N. GUPTA & J. C. DEB

White chrome lining leather produced from average quality sheep skins finds many uses in footwear and leather goods industry e.g., for white or fancy coloured shoes and ladies' hand bags. Such a leather should be full, of good feel and strength and should not discolour on ageing. Usually the leathers are produced by alum tanning. However, the leather obtained is poor in substance, feel and strength, and deteriorates on wetting and due to perspiration. With a view to eliminate these drawbacks, two low cost processes for the manufacture of white lining leather of improved quality have been worked out.

## RAW MATERIALS

Wet salted average quality sheep skins are taken. The skins are trimmed and weighed.

## SOAKING

The goods are soaked in a pit or paddle in plain water for 1½ hours. They are then broken over the beam on the flesh side with a blunt knife; the water is changed and the paddle run for another 1½ hours. The skins are then taken out and drained.

# LIMING (BY PASTE METHOD)

The unhairing is done by using a depilating paste of 1.5% sodium sulphide, 0.5% calcium chloride, 12% slaked lime and 12% water (on the raw weight). Sodium sulphide and calcium chloride are dissolved separately in hot water and the solutions are added to the slaked time. The paste is cooled down to room temperature before application. It is better to prepare the paste one day prior to the application on the skins. The paste is applied on the flesh side of the skins. The skins are then piled up flesh to flesh on a platform and kept overnight.

Next day, the skins are unhaired and put into new lime liquor containing 5% slaked lime and 300% water (on the raw weight) in a pit for two days. The goods are handled thrice every day during these two days. On the 3rd day the skins are taken out, fleshed, scudded, weighed and washed thoroughly in running water in a drum or in a pit for 20 minutes. The skins are then ready for deliming.

## DELIMING

The washed skins are delimed in a drum using 0.5% ammonium chloride and 200% water (on the fleshed weight). The drum is run for 30 minutes. The goods are taken out, scudded, put back into the same deliming bath and drummed. Then 0.5% naphthalene sulphonic acid (BASF or Coromandel Chemicals Ltd.) is added to the deliming bath; the drum is run for another 30 minutes. The skins are taken out and washed.

After deliming, two different processes are followed as described below.

## PROCESS NO. 1

## **PICKLING**

The delimed skins are pickled overnight in a drum using 4% salt, 4% alum, 0.25% formic acid, 1% sulphuric acid and 100% water (on the pelt weight). Salt and alum are first dissolved in water and the skins are put in the drum which is run for 10 minutes. Formic acid is diluted and then fed into the revolving drum through the hollow axle and the drum is run ½ hour. Sulphuric acid is diluted and then added to the drum through the hollow axle in two instalments at an interval of 30 minutes. After the last addition, the drumming is continued for 1 hour and the skins are left in the bath overnight. Next morning, the skins are drummed for 30 minutes and the pH is adjusted to 2.5-2.8. The pickled pelts are now ready for tanning.

## TANNING

Tanning is done in the pickle bath itself. The tan liquor is prepared the previous day by dissolving 4% B & C chrome extract powder. This liquor is added into the pickling drum through the hollow axle in three instalments at intervals for 1 hour. After the last adition, the skins are drummed for 2 hours. The goods are then taken out and horsed overnight. Next morning, the skins are put again in the same tanning bath and the drumming is continued for 1 hour more. The skins are then basified with 0.5% sodium bicarbonate dissolved in 50% water. The bicarbonate solution is added in three instalments at intervals of 30 minutes. After the last addition, the goods are drummed for 1 hour more. pH is adjusted to 3.5-3.6. The skins are piled up on a horse for two days.

## SAMMYING AND SHAVING

The skins are then slicked on the flesh side, sammed, shaved, weighed and are now ready for retaining.

#### RETANNING

After thorough washing, the skins are retanned with 2% Tanigan Supra LH (Farben Fabriken Bayer) or Basyntan Supra DLE (BASF) in 50% water (on the shaved weight). After drumming for 20 minutes, 0.25% oxalic acid is added and the drumming continued for one hour. The skins are then piled up. They are now ready for neutralisation and fatliquoring.

## NEUTRALISATION

The skins after thorough washing are neutralised for 45 minutes in a bath consisting of 1% sodium bicarbonate, 1% sodium acetate and 200% water (on the shaved weight). The neutralised skins are tested for proper neutralisation with bromocresol purple. Purple colour on the leather surface and yellow colour in the middle layer indicate proper neutralisation.

## WASHING AND FATLIOUORING

The neutralised skins are washed in one change of water and fatliquored with 3% T.R.O., 1.5% castor oil and 200% water (on the shaved weight). The pH of the fatliquor emulsion is adjusted to 7.8-8.0. The skins are drummed with 200% water at 50°C.

The fatliquor emulsion is then fed into the running drum through hollow axle and drumming continued for 45 minutes. The bath is fully drained. 2% titanium oxide made into a paste with a small quantity of water is added into the drum which is run for 1 hour. The skins are piled up on a horse.

#### SAMMYING AND STAKING

Next day, the skins are slicked and hooked to dry. The semidried skins are staked by machine with medium pressure and aired off. The skins are restaked with light pressure and nailed on board under moderate tension. After being kept for 4-6 hours on the board, the skins are removed and trimmed.

## **BUFFING AND FINISHING**

The skins are buffed on the flesh side with 180 grit emery paper and restaked. Then french chalk is applied on the grain side lightly. The grain is snuffed with 400 grit emery paper. The skins are measured and packed up.

## PROCESS NO. 2

This process is identical to Process No. I but in the retaining operation, 4% CLPI Syntan PC is used in place of Tanigan Supra LH

# NATURAL CHROME FOR BATTING GLOVES AND GLOVE LEATHER FOR DEFENCE FROM SHEEP SKINS

## P. C. DEWAN & S. P. GHOSH

Batting gloves have tremendous export potentiality. The sports goods industry is handicapped due to non-availability of quality leather suitable for this purpose. Formerly, the industry was getting leathers from regions which lacked the requisite qualities such as reasonable run, strength and good tannage. The process given below has helped the industry to boost their exports.

#### RAW MATERIALS

Papras and woolly sheep skins measuring 81.2-101.6 cm along the backbone.

## SOAKING

The skins are soaked as usual in plain water for 4 hours, washed in two changes of water and piled to drain excess water. The soaked weight is noted.

#### PAINTING

Painting is carried out with 1.5% sodium sulphide, 7.5% slaked lime and 15% water (on soaked weight). The skins are piled in pairs, flesh to flesh overnight.

The paste is made a day earlier before use. Next day, the skins are unhaired and put in lime bath containing 7.5% slaked lime, 100% old lime (twice used) and 300% water (on soaked weight). They are then handled twice during the day. They are now allowed to remain for 5 days in the same lime solution; hauled and replaced twice daily. The skins are now unhaired and relimed with 5% slaked lime to 300% water for two days (calculated on soaked weight). They are then taken out of the reliming bath, fleshed, scudded and washed in drum for 20 minutes after recording the fleshed weight.

## DELIMING

The skins are delimed in drum with 0.5% ammonium chloride in 150% float (on fleshed weight) for 25 minutes and bating is started when the pelt has been delimed two-thirds.

#### BATING

The skins are bated with 1% Oropon OR (Rohm) in deliming bath, maintaining a total float of 250% at 37°C for 1 hour. They are then scudded, washed and pickled.

## **PICKLING**

Pickling is carried out with 1.5% sulphuric acid (sp.gr. 1.84), 7% common salt and 100% water. The goods are run in 90% salt bath for 10 minutes and acid diluted with 10% water is added in two instalments in 40 minutes. Drumming is continued for 2 hours more and the goods are left in drum overnight. Next morning the goods are drummed for another 1.5 hours, piled and covered with polythene sheet for ageing for 7 days, taking care to see that the skins do not get dried out. The end pH of the pickle bath is 2.6 (% chemicals are based on fleshed weight).

#### **DEGREASING**

Degreasing is done with 15% kerosene oil and 1% Noigen LP (Dai-ichi Karkaria, Bombay) (on pelt weight). The goods are drummed for 1 hour. The pelts are now beamed to press the grease out.

## BRINE WASHING

(i) The skins are washed in the drum in 200% of a 10% brine solution for 45 minutes. The bath is drained. (ii) The washing is repeated in 100% float for 30 minutes. The bath is drained. A washing is now given in 5% brine using a float of 100% for 30 minutes. Two or three plain water washings follow now till the wash water becomes clear.

#### CHROME TANNING

8% B & C chrome extract powder (B & C Mills, Madras) is dissolved in warm water a day earlier in the ratio 1:3. Degreased skins are run first with 2% common salt and 60% water for 5 minutes followed by the addition of 2% alum for 30 minutes. Chrome liquor is added in three instalments at 20 minutes intervals and the goods are drummed for another 2 hours and left overnight. Next day, the goods are drummed for another 4 hours by which time the chrome liquor has penetrated thoroughly.

## **BASIFICATION**

The goods are run for one hour in the morning of the following day and basified with 1% sodium bicarbonate slowly over a period of 40 minutes followed by 1.5 hours' running. The leathers are then piled on floor and covered with polythene sheet. The end pH of chrome bath should be 4.0.

## SHAVING

The skins are sammed and shaved to level the substance and the shaved weight is recorded.

## WASHING

The goods are given two washings for 20 minutes each.

## NEUTRALISATION

The leathers are neutralised with 1.5% sodium bicarbonate in 200% water (on shaved weight) for 1.5 hours and bicarbonate is added in 4 fee is at intervals of 15 minutes. Complete neutralisation is done as tested by bromocresol green. The goods are now washed for 10 minutes.

## **FATLIQUORING**

Fatliquoring is done with 8% Fatbase G (CLRI), 3.5% T.R.O., 1.5% groundnut oil and 200% water at 60°C (on shaved weight). The pH of emulsion is adjusted to 7 by adding liquor ammonia. Fat emulsion is added twice within 15 minutes and the leathers are drummed further for 45 minutes after the last feed.

2% Tanigan Supra I.H (Bayer) (on shaved weight) is dissolved in water and added twice at 15 minutes interval. The leathers are drummed for another 20 minutes when 1.5% titanium oxide and french chalk (1:2) are added as a paste. The drum is run for another 30 minutes. The pieces are then piled. Next day, the fatliquored pieces are slicked and hung up for drying. They are dipped in water, left in pile for some time to even up the moisture, staked twice by hand, toggled for a couple of hours, buffed on the flesh and trimmed.

# WHITE CRUST SHEEP FOR CRICKET BATTING GLOVES AND 'BANDHANI' LEATHERS ETC.\*

# J. K. KHANNA & P. S. VENKATACHALAM

#### INTRODUCTION

Usually cricket batting gloves are made from chrome tanned or alum tanned sheep skins. A good percentage of these skins is not suitable for this purpose due to the presence of grain defects. Besides, a majority of these cannot be made into suede leathers, as the nap is woolly. Very often the surface is covered with white spots.

Another defect very common in sheep skins is the presence of dark patches due to non-removal of scud. It is very difficult to get a reasonably white leather especially out of black-haired wool sheep skins. Natural grease again causes patchy results. Special attention has been given to minimising the above defects by suitable modifications of the process.

## APPROACH

Unhairing is achieved by painting the flesh side with a composition made of sodium sulphide thickened with china clay. The painted skins are unhaired and relimed in sodium sulphide bath. The use of lime is avoided as it is felt that the presence of calcium soap will hinder removal of scud and interfere with subsequent dyeing. Deliming with sodium bisulphite helps to produce a brighter pelt. Addition of a nonionic detergent in bating and in the subsequent dry drumming operation helps to cleanse the pelts. They are further cleaned by an acid wash before pickling.

The defective skins can be put to profitable use by producing a floral dyeing effect on the flesh side that masks the blemishes. The Rajasthani method off tie-dyeing ('bandhani') is adopted here. Such leathers can be used for making ladies' and children's garments.

#### PROCESS

The wet salted sheep skins are weighed and soaked in a paddle containing 0.1% of sodium trichlorophenate on the raw weight of the

skins. Next day, the paddle is run for 30 minutes and the skins are cut open along the belly. The skins are washed in three changes of water and piled. The drained skins are painted on the flesh side with the following paint:

2% sodium sulphide flakes
(Travancore Chemicals Ltd.)

5% china clay

25% water

on the wet
salted weight

The skins are piled flesh to flesh and covered with wet gunny bags. Care is taken to apply a liberal quantity of the paint on the edges. Next day, the goods are unhaired on the beam and relimed with 1% sodium sulphide and 250% water.

The goods remain in this liquor for a period of 2 days. On the 3rd day, the skins are fleshed and scudded. The pelt weight is noted. A selection-is made at this stage.

The skins with very poor grain and flesh are removed and limed further for a period of 2 to 3 days and taken for vegetable tanning.

The skins selected for chrome tanning are delimed in drum with 1% sodium bisulphite and 150% water. The drum is run for 45 minutes. (If necessary 0.125% sulphuric acid (S.G. 1.83) can be used to achieve complete deliming). The delimed skins are now bated in a separate bath in a drum with 1.5% Anilobate GM (Anil Starch Co.), 0.25% Triton X 100 (Rohm & Haas) and 150% water at 37°C.

The drum is run for 2 to 2½ hours. By this time, the skins are bated. The bath is drained and the goods are dry drummed with 0.25% Triton X 100 for 15 minutes. They are now taken out, scudded and washed in plain water for 15 minutes. The skins are now washed in the drum with 0.25% acetic acid in a float of 150%.

The pelts are next pickled in a drum with 2% sulphuric acid, 15% salt and 80% water. The skins are entered in the drum with salt and water. Sulphuric acid diluted and cooled is now given in 4 feeds at intervals of 15 minutes. The drum is run for 1 hour and the skins are left immersed in the bath overnight. Next day, the goods are drummed for a further period of 15 minutes and the cut section is tested for a pH of about 2.0. The skins are piled on a horse for a period of one week.

The drained skins are now degreased in a drum with 20% kerosene oil, 1% Triton X 100 and 5% water. Half of the quantity of Triton X 100 is mixed with the kerosene. The other half is mixed with the water. Water containing Triton is now added to kerosene oil with mixing till a thick creamy emulsion is obtained. The skins are run in this bath for 1 hour. They are now taken out, beamed to remove the emulsion and grease and washed in 3 changes of brine. The 1st and 2nd washes are with 10% brine solution and the last one is with 5% brine solution. Now they are washed in plain water.

The skins are drained and tanned in a drum with 3% Tanigan 3 LN (Bayer India Ltd.), 125% water and 2% salt. The goods are run for one hour and piled. Next day, they are chrome tanned with 5% bichromate equivalent liquor. No separate float is employed. The water used for dissolving the chrome extract and for its subsequent basification will form approximately 30% on the pelt weight and this will be the ultimate float in chrome tanning.

The chrome is given in 3 instalments of 33%, 45% and 50% basicity levels respectively. Total running time is about 3½ hours. The shrinkage temperature is found to be about 105°C. The drum is now flooded with 50% water. The goods are run for 30 minutes, a second instalment of 100% water is given and the drum is run for 15 minutes. The liquor is drained and the goods are washed in the drum for 15 minutes. Finally, a wash is given with 0.25% acetic acid. The leathers are piled.

Next day, they are washed and neutralised to a pH of about 6 with 2% sodium acetate and 150% water. The drum is run for 45 minutes. The goods are washed and fatliquored with 5% sulphated groundnut oil, 1% raw coconut oil, 0.25% pine tar 40 (Camphor & Allied Products) and 125% water at 50°C.

The leathers are run for 45 minutes at the end of which period 0.5% Tanigan 3LN (Bayer India Ltd.) is added. The drum is run for 15 minutes and drained. They are now drummed with a slurry of 2% china clay and 0.1% Titanium-dioxide. Next day, the skins are sammed, set and hooked to dry. When they have dried out, they are saw-dusted in fresh saw dust or dipped in water and piled. Next day, they are staked, dry drummed in a clean drum for 3 to 4 hours and restaked.

The pieces are now trimmed and assorted.

is now put into the drum and the drum run for 10 minutes. The leathers are horsed overnight. Next day they are struck out, sammed, set out and dried. When completely dry, they are aged for 3 days, conditioned in the usual way, staked, nailed on boards and dried. The dried leathers are trimmed and buffed on the flesh side with 180 grit emery paper and on the grain side with 320 and 400 grit papers. The buffed leathers are brushed and are ready for the decalomania application.

## DECALOMANIA APPLICATION

A white pigment finish is prepared with 1 part white pigment paste, 2 parts acrylic co-polymer emulsion (40% solids) and 4 parts water. The finish is applied on the grain side twice by brush or pad, drying in between. In certain cases a spray coat of the resin emulsion diluted four times, over the pigment coat is helpful. The leather is aired off after this application of finish. The decalomania paper having the design required to be transferred is put on the grain side with, of course, the design in contact with leather. The assembly of decalomania and leather is plated at 190-195°F. The press is now closed and kept in the closed state for about 15 seconds. The most important point is to avoid air bubbles and folds. Air must be allowed to go off during the lamination. Any fold or wrinkle allowed to be developed cannot be rectified easily later.

Where a hydraulic press is not available, a hand iron may be used. Small sections must be ironed gradually eliminating air. Great care and skill is necessary when using hand iron. Due to the heat employed, the adhesive used on the decalomania becomes plastic and releases the design from the paper. So it is necessary that the temperature employed be sufficiently high as to release the design.

When the paper becomes well fixed on to the leather without any fold or wrinkle and is quite flat it can be assumed that the transfer had been well made. Now water is sprayed on the surface of paper so as to soak it. When sufficient water is sprayed, the paper automatically lifts itself up and is peeled off. Now the leather is air dried and a nitrocellulose lacquer is sprayed on the decalomania coated surface. After the lacquer spray, leather is dried and trimmed. This completes the process.

Very attractive leathers have been prepared in this manner depending, of course, on the design on the decalomania.

# I(b) FINISHING OF SPLITS WITH DECALOMANIA

Splits from the splitting machine are assorted and shaved to level substance. Thin areas of substance below 0.5 mm. are cut off. Shaved splits are loaded in a drum with a float of 200% water, run for 20 minutes and drained. The wash is repeated once again, the bath drained and stock refloated with 200% water. 1% sodium bicarbonate is added in 3 feeds at 10 minutes' intervals and the drum run for another 20 minutes and drained. pH of cut edge should be 4.5-5.5 as checked by Bromocresol Green. The goods are washed once with 200% water and drained. Stock is refloated in 150% water at 70°C and fatliquored with 5% CLRI FATBASE F for 30°. The splits are pulled out and piled. A thick paste of 3% corn flour in 30% water is made by cooking. 5% china clay is added and the stock run in this paste for 20 minutes. The splits are pulled out, dried, aged for 2 days, conditioned as usual, staked and tacked on boards to dry. After drying they are trimmed and buffed with 180, 240 and 400 grit emery papers on the side to be finished and with 180 grit emery papers only on the rough side. On the side to be finished buffing should be quite close and there should be no raised Buffed surface must be smooth.

After buffing, the leather may be decorated with decalomania as described for grain leathers.

## II. HAND PRINTING OF LEATHER

Leathers can be printed in many designs and colours as in the textile industry using wooden blocks. Attractive finishing can be done even on poor quality leathers.

Inferior rejections of E.I. sheep skins are shaved level and buffed on the grain with 320 paper. The buffing dust is brushed off and the leathers are stained with a 2% solution of Naphthalene orange G.S. (ICI) acidified with half its weight of formic acid. Then the leather is dried and is ready for printing.

Pigment pastes of blue, red, white and green colours are prepared in order to print a flower design. The finish is composed of 1 part water pigment paste and 14 parts acrylic polymer emulsion.

Pastes of the different colours are poured over felt pads covered with fine cloth to prevent the felt fibres coming off when the blocks are pressed on them. The component blocks are pressed on

the appropriate colour pads and printed on leather. Care is taken to avoid crowding of the prints. A mark is made on the block to see that it is not reversed. Each component block in a design has to be fitted in its proper place. Single colour printing takes much less time than multi-coloured. The proper positioning of the component blocks is easily mastered after a few trials.

When the entire leather surface is covered with the design, the leather is trimmed and topped with a nitrocellulose lacquer. The leather is aired off well until the lacquer is well dried. This completes the process.

Thus attractive designs may be put on even inferior quality leathers so as to increase the sale value of such leathers.

# FANCY LEATHER FOR LEATHER GOODS FROM CHROME AND VEGETABLE TANNED SPLITS

J. C. DEB

Using resin binder and pigment, chrome and vegetable tanned splits may be finished in attractive and pleasing colours. Leathers so finished could be used for making economically priced leather goods like suit cases, traveller's box, portfolios, zip cases, jewellery cases, camera cases, etc. Such leathers varying from 1.0-1.5 mm. in thickness are being regularly used in the leather goods industry. The qualities required in the finished splits are softness, pliability, strength, non-stretchiness, fast colour, non-crackiness on double fold and fastness to light. This field is one which can be profitably explored and exploited by the Indian tanner.

#### RAW MATERIALS

Chrome tanned splits are assorted and shaved to a level substance 1.0-1.5 mm. The splits of different thickness could be used for different types of leather goods. The shaved weight of the splits is recorded.

## WASHING AND RETANNING

The shaved splits are drummed in a large float of water for 30 minutes and rested overnight. Next morning, the drum is drained. 3% chrome extract powder dissolved the previous day in 100% hot water (on the shaved weight) is taken in the drum along with the splits and drummed for 3 hours. At this stage, basification is effected with 1% soda ash dissolved in a small quantity of water. The drum is run for one more hour and the goods are horsed up.

## NEUTRALISATION

The retanned splits are washed in a drum with 300% water (on the shaved weight) for 15 minutes and then neutralised in a fresh float (300%) with 2% ammonium chloride and 1% soda ash for 45 minutes. Neutralisation should be complete as tested by bromocresol purple-indicator. They are then washed with 500% water for 15 minutes. The goods are then removed and are ready for pearling and fatliquoring.

## PEARLING AND FATLIQUORING

The goods are fatliquored in a bath made up of 2.5% sulphated fish oil 2.5% T.R.O., 3% china clay, 2% flour (cooked in water) and then buffed first with 80 grit emery paper on both sides and then horsed.

#### TOGGLING AND DRYING

The splits are toggled or nailed on board and dried completely.

# SAW-DUSTING, STAKING, BUFFING AND DRUMMING

The dried splits are damped back by keeping them in moist sawdust for 2-3 hours, staked with heavy pressure, hung up to dry and then buffed first with 80 grit emery paper on both sides and them with 320 grit paper on the split side only. They are then dusted off, trimmed and are ready for finishing.

# B. VEGETABLE TANNED SPLITS

#### RAW MATERIALS

Vegetable tanned splits are assorted and dry shaved to level substance 1.0-1.5 mm. The shaved weight of the splits is recorded.

## WASHING AND STRIPPING

The shaved splits are washed in a drum with a good float for 15 minutes and left in the drum overnight. Next morning, the float is drained out and the stock is stripped with 300% water and 2% borax for 30 minutes. This is followed by a wash in a liberal float for 15 minutes. The splits are now horsed to drain.

## CHROME TANNING

6% chrome extract powder is dissolved in 100% hot water a day prior to its use. The splits are put into the tanning drum with 100% water and half the quantity of the chrome liquor. The other half of the liquor is added after running the drum for 30 minutes. After drumming for three more hours, basification is done with 0.5-1.0% soda ash dissolved in a small quantity of water. Drumming is continued for 3-1 hour and then the goods are taken out and horsed.

## NEUTRALISATION

The chrome tanned splits are washed in a drum with 400% water for 15 minutes and then the bath is drained. A fresh bath is prepared with 300% water, 2% ammonium chloride and 1% soda ash

and the goods are run in this bath for  $\S$ -1 hour. Neutralisation should be complete as tested with bromocresol purple. This is followed by another wash in 500% water for 15 minutes. The leathers are then removed and are ready for pearling and fatliquoring.

## PEARLING AND FATLIQUORING

The splits are put into a drum with a float of 200% water at 50°C. 2.5% flour is cooked in a small quantity of water and mixed with 2.5% china clay, 2% sulphated fish oil and 2% T.R.O. This mixture in emulsion form is then added through the hollow axle into the revolving drum which is run for one hour. The goods are then removed and horsed up.

#### FINISHING

The following procedure is adopted for both chrome and vegetable tanned splits.

## 1. COLOURED PRINTED LEATHERS

Bottom season: It is prepared with 3 lb. pigment paste to match shade, 8 oz. CLRI Binder A, 3 lb. synthetic resin emultion, 2 oz. ammonia, 2 oz. T.R.O. and water to make up to 1 gallon. The coat is applied twice with pad on the split side and then allowed to dry. The dried splits are then smooth-plated at 150°F with medium pressure. One pad coat and one spray coat are then applied and the splits allowed to dry.

Fixing coat: The fixing coat made up of 1 part 10% casein solution, 1 part 40% neutral formaldehyde and 4 parts water is sprayed liberally and then allowed to dry. The splits are then embossed with the desired design at 100°F with full pressure.

Alternately a lacquer top may also be given to render the film water-resistant.

Clear top lacquer coat: Clear lacquer consists of 1 part spartan clear lacquer (Addison & Co.) and 3 parts spartan thinner. Four cross coats are sprayed to make the leathers completely fast to wet and dry rubbing.

The finished leathers are then measured and smooth plated at 150°F with light pressure. They are then ready for assortment.

Bottom season: It is prepared with 2.75 lb. pigment paste to match shade, 6 oz. CLRI Binder A, 1½ oz. ammonia, 1½ oz. T.R.O., 2¾ lb. synthetic resin emulsion and water to make ¾ gal. Two pad coats of the season are applied on the splits and then allowed to dry. The dried splits are smooth-plated at 150°F with medium pressure. One pad coat and spray coat are then applied and the leathers are allowed to dry.

Top colouring coat: 2 lb. pigment paste of darker blue than the bottom and 8 lb. water are used in this composition. A spray coat is given and the leathers are allowed to dry.

Fixing coat: A spray coat of the fixing coat consisting of I part 10% casein solution, neutral and 4 parts water, is given and the leathers are allowed to dry. The dried splits are then embossed with a suitable design at 150°F under full pressure. The embossed splits are then cleaned by rubbing with a wet cloth pad, which is first dipped in 5% ammonia solution and the excess solution wrung off. The two-tone effect is thus produced with the bottom shade showing on the raised portions of the embossed leather and the top colour in the valleys. The cleansed splits are then dried, topped with a lacquer coat and then finished as given under coloured printed leathers.

V. RANGA RAO, T. S. KRISHNAN & P. S. VENKATACHALAM

Split leathers produced as a by-product in the tanning of grain leathers from cow and buff hides can be processed into a variety of finished leathers like shoe suedes, industrial gloves, welders' gloves, plain or printed upper and lining, laminated leathers, etc. The splits generally vary in size, thickness, degree and type of tannage as well as in quality and as such assortment should be done for their suitability for the different end purposes. The entire stock of splits should be brought to as uniform a condition as possible as the splits of the different lots will vary in pH, total acid content and chrome oxide content depending upon the original tannage and the duration of storage. Rechroming the splits prior to further processing will make them more uniform ensuring the elimination of poorly tanned areas, a common feature of splits.

Care should be taken to see that the splits are always kept in wet condition prior to processing. In case of prolonged storage in wet condition, it is necessary to treat them with preservative or to keep them immersed in used chrome liquor so as to avoid mould growth which can result in permanent discolouration.

Splits for shoe suedes should have good substance and they should be free from vein marks, flay cut, chatters due to fleshing machine and from marks of splitting machine. Hard and bony splits should also be eliminated.

# PROCESSING OF SHOE SUEDES FROM ASSORTED STOCK

Sam, shave on both sides to level substance and weigh. (Formulations are based on shaved weight).

## WASH

in drum 200% water

Run for 15 minutes-Drain

(Addition of 0.2% acetic acid in washing is suggested in the case of hard water)

Fancy-9

## RECHROME

50-60% water at 45°C

Add chrome liquor (40% basic)

containing 1 to 1.25% Cr.O.

Run for 1 hour.

Basify by adding enough soda bicarb. dissolved in water (10%) in several slow feeds during a period of 45 to 60 minutes.

Run finally for 1 hour.

End pH should be 4 to 4.2.

(The amount of soda bicarb. will depend upon the acid content of the splits.)

Drain-Horse up overnight.

## WASH

300% water Run for 20 minutes—Drain.

## NEUTRALISE

150% water.

Add 0.75% Ammonium sulfate + 10% water.

Run for 15 minutes.

Add 2 to 2.5% neutralising agent consisting of equal parts soda ash and soda bicarb. + 30 to 40% water in 4 or 5 feeds at intervals of 30 minutes.

Run finally for 1½ hours. Add 200% water—Run for 10'. Leave the goods in the bath overnight, well immersed. Next day run for 20 to 30 minutes. Check pH of cut edge. (The pH of cut edge should be 6 through and through.)

#### WASH

300% water at 45°C. Run for 10 minutes—Drain.

#### WASH

300% water at 55°C.

Run for 10 minutes—Drain.

## **FATLIQUOR**

100-125% water at 55°C.

Add 7.5% Sandozol KBS (Sandoz India).

0.5%Raw Groundnut oil.

0.5% Teepol B 300 (Shell chemicals) emulsified with hot water (1:3) in 2 feeds at intervals of 10.

Run finally for one hour.

Check exhaust.

Sometimes formic acid upto ½% is required to produce better fatliquor takeup. The acid is diluted (1:10) with water and added in 2 or 3 feeds at intervals of 5' and the drum is finally run for 10 to 15 minutes.

Drain 2/3 float.

Add 1.5% china clay made into a paste.

Run for 20 minutes-drain.

Horse up overnight.

Hook to dry-crust for a few days.

Saw-dust overnight—Dry drum for 2 to 3 hours—Stake if possible—Air off to dry

Buff on both sides with 150 grit paper followed by 240, 320 grit papers.

Brush-Assort-Weigh.

# DYEING OF SPLITS: (All formulations based on dry buffed weight)

#### WET BACK IN DRUM

800% water at 60°C.

Add 1.5% ammonia + 1.0% Sandozin NIS (Sandoz)

01

auitable nonionic wetting agent + 10% water

Run for 1½ hours—Leave in bath overnight.

Next day run for 20'-Drain,

#### WASH

800% water at 60°C.

Run for 15'-Drain.

## DYE (Olive Green)

400-500% water at 60°C.

Add 1.0% ammonia + 10% water.

Run for 10 minutes.

Add 1-2% Sandozol KBS

emulsified with hot water (1:3)

Run for 15'.

Add 2/3 the total dve in 2 feeds at intervals of 10'.

Run finally for 11 hours.

Add 1.75% formic acid (85%) + 25% water

in 3 feeds at intervals of 5'.

Add 1/3 (remaining) dyc

Run for 20 minutes.

Add 1% formic acid + 15% water in 3 feeds at intervals of 5'.

Run finally for 20 to 30 minutes.

Check exhaust-Drain.

Rinse well in cold water for 5 minutes. Horse up overnight.

# DYE COMPOSITION (Olive Green)

Sandopel Bronze B (Sandoz)-3%

Chlorazol Orange PO conc. (ICI)-0.75%

Chlorazol dark green PLS (ICI)-0.25%

Dissolve the dye in hot water (1:40) and filter.

# DYE (Black)

400% water at 60°C

Add 1.0% ammonia + 10% water

Run for 10 minutes.

Add 1% Sandozol KBS

emulsified with hot water (1:3)

Run for 10 minutes.

Add 2.0% Atul Direct Black E Extra High Conc. (Atul)

+0.66% Derma Carbon GTS 200% (Sandoz)

+0.5% Chlorazol Dark Green PLS (ICI).

+ Hot water to dissolve (1:40).

in 2 feeds at intervals of 10.

Run finally for 11-11 hours.

Add 2.0% formic acid + 30% water

in 3 feeds at intervals of 5'.

Run finally for 15'.

Add 1.5% Atul Direct Black E Extra High Conc.

+ 0.5% Derma Carbon GTS 200

+ Hot water to dissolve (1:40).

Run for 30 minutes.

Add 2% acid formic + 30% water in 3 feeds at intervals of 5'.

Run finally for 30 minutes.

Check exhaust-Drain.

#### RINSING.

800% water at 50°C

Run for 5'-Drain.

#### BASIC TOPING

500%-600% water at 50°C.

Add 3.7% Basic dye mixture (CLRI)

+ 2.75% acid acetic.

+ Hot water to dissolve (1:40)

in 2 feeds at intervals of 10.

Run finally for 30 minutes.

Add 0.5% ammonia

+ 0.5% Sandozol KBS

+ 5% water

in 2 feeds at intervals of 5'.

Run finally for 15 minutes.

Check exhaust—Drain.

#### RINSE

600% water.

Run for 5'—Drain—Horse up.

In case additional fatliquoring is necessary, rinse in hot water at 50°C and fatliquor in a separate bath using 1 to 1.5% Sandozol KBS.

## DYE (Brown)

400-500% water at 60°C.

Add 1.0% ammonia

+ 10% water.

Run for 10'.

Add 1 to 2% Sandozol KBS

emulsified with hot water (1:3)

Run for 15'.

Add 1.0% Naphthalene Leather Brown ADS (ICI)

0.6% Coomassie Navy Blue 2RNS (ICI)

0.6%Chlorazol Brown MS (ICI)

+ Hot water to dissolve (1:40)

in 2 feeds at intervals of 10'.

Run finally for 1½ hours.

Add 2% formic acid

+ 20% water

in 3 feeds at intervals of 5'.

Run finally for 20 to 30 minutes.

Check exhaust-Drain.

#### RINSE

600% water at 50°C.

Run for 5'-Drain.

#### BASIC TOPING

500% water at 50°C.

Add 0.75% Mismark Brown RLNS (ICI)

0.1875% Methylene Blue 2B Conc (ICI)

0.075% Auromine 0 (ICI)

0.75% acetic acid

dissolved in hot water (1:40)

Run for 30 minutes-Check exhaust-Drain.

#### RINSE

600% water at 55°C.

Run for 5'-Drain,

#### TOP DYE

400-500% water at 55°C
Add 1% Dermalight Brown GRL (Sandoz)
0.3% Chlorazol Orange PO Conc. (ICI)
0.15% Chlorazol dark green PLS (ICI)
dissolved in hot water (1:40)
Run for 25 minutes
Add 1.0% Formic acid
+ 15% water
in 2 feeds at intervals of 5'
Run finally for 20-30 minutes.
Check exhaust—Drain.

#### RINSE

800% water

Run for 5'-Drain

Horse up overnight.

The dyed and horsed up skins are hooked to dry, crusted for a few days, saw-dusted overnight, dry drummed till the nap is opened up and aired off.

They are then measured and assorted.

# SPRAYS FOR DEEPENING THE SHADE (if necessary)

(i) 5 parts Glycerine 15 parts Spirit 85 parts Water

or (ii) 5 parts Glycerine
5 parts T.R.O.
15 parts Spirit
70 parts Water

or (iii) 5 parts Basic or anionic dye (adjusted to shade)
5 parts Acetic acid (in case of basic dye)
50 parts Glycerine

80 parts Spirit

Water to make 1 litre.

One or 2 cross coats of the above spraying seasons are given, dried and the splits are dry drummed, if necessary.

The spray season (i) and (ii) have a purely optical effect whereas by (iii) the correction of the shade is also possible besides deepening the shade. For improving crock resistance, a light spray coat of (2% solid) acrylic resin solution in water may be given although it may make the nap slightly harsh.

#### Note:

- (i) For getting a soft crust, the splits should be in wet condition prior to processing. Rechroming and thorough neutralisation are quite necessary for producing a split with the proper feel besides the quantity of suitable fatliquor.
- (ii) Ammonium bicarbonate may be used for neutralising as it will help in quicker and thorough neutralisation.
- (iii) Use of Syntan PN (Allied Resins) upto 2 or 3% in neutralisation will help not only in quicker neutralisation but also in filling up the splits to some extent.
- (iv) Where more fullness is required 3 to 5% wattle extract may be added during dyeing operation prior to the addition of fat-liquor. But this will affect the depth of shade to some extent.
- (v) A softer crust will be obtained by replacing half the amount of Sandozol KBS with sulphonated fish oil, in initial fatliquoring.
- (vi) As the margin of profit in split processing may be very little, proper care should be taken in economising the process. Depending upon the price obtainable and the choice of the consumers, quantities of dyes may be decreased or increased.
- (vii) Instead of formic acid a mixture of acetic acid and sulphuric acid 19:1 on volume basis may be tried as formic acid is generally costly.
- (viii) The composition of basic black mixture (CLRI) will be given on request.
- (ix) The splits from buff hides are inclined to be loose with woolly nap.
- (x) Instead of drying completely after initial fatliquoring, the splits may be removed during drying in a slightly humid condition and straightaway dry drummed to soften them.
- (xi) The process is given in good faith after repeated trials in our fannery
- (xii) In the place of Sandozol KBS, any other suitable fatliquor may be used.

#### TWO-TONE SUEDE LEATHER FROM CHROME SPLITS

K. B. GUPTA, D. H. KAMAT, K. T. SARKAR & M. ROY CHOWDHURY

#### INTRODUCTION

Two-tone suede also known as Angora suede is popular for making goods and sandals in the European market. The splits should be soft and produce a long-fibred nap. An understanding of the penetration and dry-rub fastness properties of the dyes used is important to produce a successful two-tone dyeing.

#### RAW MATERIAL

Chrome tanned splits of buffalo and cow hides of area one sq. ft. or more and of minimum thickness 0.8 mm. are trimmed to remove holes and very thin portions.

#### SHAVING

The splits are shaved on the flesh and upper sides to a uniform thickness. Heavy splits above 1.5 mm. thickness are shaved to 1.2-1.3 mm. thickness. The shaved weight is noted. (The percentages of chemicals given are on the shaved weight).

#### FIRST DAY

#### WASHING

The splits are washed with 500% water for 15 minutes; the bath is drained.

#### BLRACHING

To bring the stock to uniform light colour, the splits are lightly bleached by drumming for 30 minutes with 100% water and 0.5% sodium blaulphite, followed by drumming for 30 minutes more after adding 0.25% oxalic acid in 20% water. The bath is drained.

#### WASHING

The splits are washed with 500% water for 10 minutes and the bath is drained.

Fancy-10

#### RECHROMING

The splits are rechromed with 6% B & C chrome power (50% basicity) and 30% water, the drum being run for 1 hour. After adding 70% water at 50°C, the drum is run for 30 minutes. The pH of the bath is adjusted to 3.7-3.8 by adding 0.3°5% soda bicarbonate in 10% water and running the drum for 30 minutes. The float is drained and the splits are rinsed in water and piled overnight on a wooden horse.

#### SECOND DAY

#### **NEUTRALISATION**

The splits are drummed for 20 minutes with 80% water and 0.5% soda bicarbonate. After adding 0.5% soda bicarbonate + 10% water, the drum is run for 15 minutes. The addition of 0.5% soda bicarbonate in 10% water and drumming for 15 minutes are repeated thrice. The neutralisation is carried out to a uniform pH 6.0-6.2 throughout the section of the leather, tested with bromocresol purple. In case the neutralisation is not upto this mark, the same can be achieved by addition of 0.25-0.5% liquor ammonia in 10-15% water and drumming for 15 minutes. The bath is drained.

1st washing is with 300% water for 10 minutes; the bath is drained.

2nd washing is with 300% water at 40°C for 10 minutes; the bath is drained.

#### **FATLIQUORING**

A mixture of 6% T.R.O. (highly sulphated), 1% Lipoderm Liquor II (BASF India) or any other sulphated sperm oil, 1% raw groundnut oil, 0.5% glycerine, 0.5% Monogen I.OC (Dai Ichi) 0.5% Pine Tar — 40 (Camphor and Allied Products) and 100% water at 55°C is added to the neutralised and washed stock and the drum is run for 45 minutes. After adding 1% Basyntan DI (BASF India) and 10% water, drumming is continued for 15 minutes. Next 1-1.5% formic acid in 10-15% water is added and the drum run for 15 minutes and exhaustion of fatliquor bath is checked.

Next 0.001% Tinopal WB (Suhrid Geigy) in 10% water (40°C) is added and the drum run for 15 minutes. The bath is drained.

The splits are piled for 3-4 hours on a wooden horse and then hooked up for drying. When the leathers are dried, they are conditioned in sawdust, staked, dry drummed for 4 hours, loosely toggle dried, trimmed, buffed on both the sides with 100, 150 and 240 grit emery papers and brushed; the crust weight is noted. Percentages of chemicals given hereafter are on crust weight

#### WETTING

1% Liquor ammonia, 800-1000% water (40°C) and 1% Teepol B 300 (Shell Co.) are added and the drum is run for 3-4 hours till the splits are thoroughly wetted back. The bath is drained

#### WASHING

The splits are washed by drumming for 10 minutes with 1000% water at 40°C. The bath is drained. The splits are dyed as described below:

## BOTTOM-DYEING

This is carried out with 300% water at 50°C, 0.5% diethylene glycol and 1% T.R.O., the drum being run for 15 minutes. Next 0.5% liquor ammonia in 10% water is added and the drum run for 10 minutes. Next 4% acid dye (penetrative type) of lighter shade (e.g. yellow, light brown, orange, light red etc.) in 50% water at 55°C is added and the drum run for 45-60 minutes, till the dye has penetrated. Next 4% acetic acid in 40% water is added to the running drum in 2-3 feeds at intervals of 10 minutes. To the same bath 0.5% Tinofix I.W(Suhrid Geigy) (or any other cationic dye fixative) in 10% water is now added and the drum run for 10 minutes; the bath is drained.

#### TOP DYEING

Top dyeing is carried out in a fresh bath with dyes of dark colours (e.g. violet, blue or dark green etc.). After adding 2-3% direct or premetallised dye (having lesser penetration) and 500% water at 55°C, the drum is run for 15 minutes. Next 0.5% Nopcolene RM (Nopco India) in 10-15% water at 50°C is added and the drum run for 15 minutes. The bath is drained. The leathers are piled on a wooden horse. After 3-4 hours, they are hooked for drying. When dry, they are conditioned in sawdust, staked, dry drummed for 2-3 hours and loosely toggle dried for 1-2 hours.

#### COMBING OF DYED LEATHERS

To obtain fibres of two different shades, the dyed suede splits are placed on a flat wooden table and combed with a densely fixed fine brass wire brush. The leathers are first combed upwar is and then downwards and finally in all directions so as to pull out he leather fibres of dark and light colours. The leathers are combed till fibres of 4-5 mm. length come out. Finally the area is measured and the leathers are brushed.

This type of two tone suede leathers can be used in the manufacture of ladies' handbags, straps for chappals, waist belts and a variety of other fancy leather goods.

# INDUSTRIAL GLOVING LEATHER FROM BUFFALO SPLITS

# R. S. GHOSH, S. N. GUPTA & A. GANESAN

The process given below covers the manufacture of industrial gloving leather from splits obtained as bye-product in the manufacture of buffalo shrunken grain leather. There is increasing demand in the country for industrial gloves and there are indications of good export prospects also.

#### RAW MATERIALS

Wet salted buffalo hides weighing 17-20 kg (35-40 lb.) per piece are taken. They are limed for 6 days with 400% old lime liquor, 1.0% sodium sulphide, 5% slaked lime and 0.25% calcium chloride, unhaired and relimed for two more days with 10% slaked lime. The hides are then split; the grain splits are taken for shrunken grain side leather; the flesh splits of thickness 2.0-2.5 mm. are suitable for industrial gloving leather.

#### RELIMING

The splits are weighed and put into lime liquor in a pit containing 5% slaked lime and 400% water (on the limed split weight). The goods are kept in this liquor for 2 days and handled daily.

#### DELIMING

The splits are washed in a drum with sufficient water for 30 minutes and then delimed with 1% ammonium chloride and 50% water (on the split weight). The drum is run for about 45 minutes to complete deliming. The goods are washed in the drum for 15 minutes.

#### PICKLING

The splits are pickled with 1.5% sulphuric acid, 0.5% naphthalene sulphonic acid (BASF or Coromandal Chemicals), 12% salt and 100% water (on the split weight). The goods are drummed for one hour and left in the bath overnight. Next day, the drum is again run for one hour.

#### DEPICKLING

The goods are depickled in a fresh bath consisting of 4% hypo and 50% exhaust pickle bath (on the split weight). The stock is taken

in a drum containing the required amount of exhaust pickle bath and the hypo is added in the solid form. The drum is run for one hour and the splits are left in it overnight. Next day, the drum is run for one hour and they are taken out, piled up and kept for 2 days for ageing.

#### ACIDIFICATION AND CHROME TANNING

The depickled splits are drummed for 30 minutes in a drum containing 0.25% formic acid, 3% salt and 100% water (on the split weight). Then 33\frac{1}{3}\% basic chrome liquor containing 2.5% Cr2O3 on the split weight is added to the same bath in three instalments at intervals of 30 minutes each. The drum is run for two hours after the last addition and the goods are left in the bath overnight. Next day, the goods are basified with 2% soda bicarbonate (on the split weight) added in six instalments over a period of four hours. The pieces are then piled up and aged for 2 days.

#### SAMMYING AND SHAVING

The splits are sammed and shaved to a thickness of 1.5-1.75 mm. according to requirements and weighed.

#### NEUTRALISATION

They are washed for 30 minutes in a drum, neutralised completely with 1.5% sodium bicarbonate (pH 6-7) and 300% water (on the shaved weight) and washed again for 30 minutes.

# **FATLIQUORING**

Fatliquoring is done with 5% sulphonated fish oil, 4% sulphonated castor oil, 1% raw fish oil, 3% tallow, 1% kerosene, 0.2% Sandozin NI (Sandoz India Ltd.) and 200% water at 70°C (on the shaved weight). The tallow is first melted and kerosene mixed with it. Sulphonated and free oils are then added to this mixture and an emulsion is made using water at 80°C. The splits are taken in the drum along with the float and the emulsion is added in one instalment. The drum is run for one hour and the bath is exhausted by using 0.5% acetic acid on the shaved weight. The goods are then piled up.

#### STAKING AND BUFFING

The leathers are semi-dried, staked and then dried completely. They are again staked in order to get the required softness.

The pieces are then trimmed, buffed on both the sides and measured.

# NOVO PRINT SUEDE LEATHER FROM E.I. TANNED GOAT SKINS

D. H. KAMAT, K. B. GUPTA & K. T. SARKAR

#### RAW MATERIAL

E.I. tanned goat skins with grain defects may be taken. The skins are buffed on the flesh and grain sides with 150 and 240 grit emery papers and the crust weight is noted (the percentages given below are on crust weight).

#### WASHING & STRIPPING

The skins are washed in 600% water in a drum for 30 minutes, drained and rinsed in water again.

The stripping is carried out for 40 minutes with 1% soda bicarbonate, 0.5% sodium sulphite and 500% water. The skins are washed with 500% water for 10 minutes.

#### SOURING

The skins are soured for 40 minutes with 0.5% formic acid, 0.25% oxalic acid in 400% water and washed with 500% water for 20 minutes.

#### CHROME TANNING

8% chrome extract powder (25% Cr<sub>2</sub>O<sub>3</sub>) dissolved in 100% water is adjusted to 50% basicity with the requisite quantity of soda bicarbonate or soda ash and left overnight. Next day, the skins are drummed in this liquor for 30 minutes after which 1% sulphited sperm oil in 10% water is added. The drum is further run for 1½ hours, flooded with 400% water at 50°C and run for 15 minutes and the goods are piled overnight. Next day, they are washed in 500% water and 0.1% acetic acid for 10 minutes.

#### **NEUTRALISATION**

The skins are neutralised for 30 minutes with 400% water, 0.75% sodium bicarbonate after which 1.25% sodium formate, dissolved in 50% water is added. The drum is further run for 45 minutes. The

pH of leather is adjusted to 5.8-6.0 (tested with bromocresol purple) and the skins are washed with 500% water at 55°C for 15 minutes.

#### **FATLIQUORING**

The fatliquoring is carried out for 40 minutes with 3% sulphonated groundnut oil, 3% highly sulphated castor oil, 0.5% polyethylene glycol 600 (NOCIL, 0.5% pinetar 40 (Camphor and allied products), 0.25% Monogen L70 (Chika Ltd.) and 200% water at 55-60°C. The fatliquor is exhausted with 1-1.5% formic acid diluted in 10-15% water, added in 3 feeds at intervals of 10 minutes. To the same drum is added 0.25% Tanigan 3LN (Bayer India Ltd.) dissolved in 10% water and run for 10 minutes. The skins are then rinsed in water and piled. Next day, the skins are hooked up for drying. When dry, they are conditioned in sawdust, staked, dry drummed for 3-4 hours, toggle dried, trimmed, buffed with 150,240 and 320 grit emery papers on both the flesh and grain sides, brushed and weighed (the percentages given below are on this crust weight).

The leathers are wetted back in a drum for 3 hours with 1000% water and 1% Noigen LS (Chika Ltd.), washed and taken for dyeing.

#### DYEING, SANDWITCH METHOD

The leathers are run in a drum for 15 minutes with 300% water at 50°C and 1.5% liquor ammonia to which is then added 1% highly sulphonated castor oil, 1% sulphonated groundnut oil, 0.1% Monogen L70 and 50% water at 50°C. The drum is run for 15 minutes after which 3% dye (acid or direct dye with good penetration and light fastness properties) is added in 50% water at 60°C. The drum is run for 45 minutes. The dye is then exhausted with 3% formic acid in 20% water added in 2 instalments at an interval of 15 minutes. Finally, 1% dye is added in 25% water at 55°C and the drum is run for 20 minutes. The dye is exhausted with 1% formic acid diluted with water, in 10 minutes. To the same dye bath is added 0.5% Dermafix or Sandofix (Sandoz India Ltd.) or Amigen L (Chika Ltd.) diluted in 10% water for 10 minutes. The leathers are washed in 400% water at 40°C.

#### TOP DYEING

The top dyeing is carried out for 10 minutes with 1-2% dye (depending upon the darkness of shade required) and 400% water at 55°C and exhausted with 1.2% formic acid diluted in 10% water for 10 minutes. The leathers are taken out, rinsed warm water and hooked up for samming. In the sammed condition, the leathers are

slickered lightly on flesh side and toggled for 10-15 minutes to remove creases and folds. In a slightly sammed condition (moisture 20-30%) leathers are printed on the suede side in a hydraulic press.

Care is taken to keep the leathers flat without wrinkles and folds while printing and a pressure of 110-150 kg./sq.cm. at 125°F is applied for half to one minute. The leathers are then hooked up for drying. When dry, they are buffed on the suede (printed side) with 150 and 240 emery papers to produce a two tone effect. The leathers are brushed, wetted back and lightly dyed with 0.5% dye (the base colour) to improve the brightness and contrast, in 300% water at 55°C. To the same bath is added ½% formic acid and 0.25% Amigen L in 10% water for 15 minutes and if desired, the leather is made showerproof by treatment in the same bath with 2% chrome stearato chloride in 10% water for 15 minutes. The leathers are finally rinsed in water and hooked up for drying. When dry, they are conditioned in sawdust, staked lightly on a hand staker, dry drummed for 5-6 hours, toggle dried, trimmed, brushed and area measured.

This type of leather can be used for making garments, belts, wallets, hand bags, ladies' shoes and other fancy articles.

Also leathers have been produced in bulk and supplied to the leather goods division of the Institute.

# CREATION OF MOTTLED AND OTHER SPECIAL EFFECIS ON E.I. TANNED GOAT AND SHEEP SKINS

# K. RAJABATHAR & M. S. OLIVANNAN

Printing coloured designs on leathers is widely employed in many countries. Several processes by which different mottled and other special effects could be developed on the tanned leathers are described here. The designs are very attractive and pleasing. These leathers are largely used in book-binding, manufacture of ladies' hand bags, boxes and cases, gents' wallets and children shoes etc.

#### RAW MATERIALS

E.I. tanned goat and sheep skins are used to meet the various requirements. For making book-binding leather, the skins should be free from flay cuts, holes, grain damage and, as far as possible, free from major defects. For other items, the skins selected should be free from grain damage. It is better to select skins of suitable sizes, preferably with thinner substance.

# PRELIMINARY TREATMENTS

The skins are weighed, dipped in water and piled preferably overnight. Next day, they are shaved to 0.5 mm. thickness carefully avoiding cuts and iron stains. They are then bleached, if necessary, using a mixture of calgon, oxalic acid and a suitable syntan adopting any one of the following formulations.

Formulation I: 400% water, 0.25% calgon, 0.25% oxalic acid and 0.75% Syntan NC (a CLRI bleaching syntan).

Formulation II: 400% water, 0.25% oxalic acid and 1.0% Syntan NC.

Formulation III: 400% water and 0.5% oxalic acid.

The skins are handled in a tub for about 10-20 minutes when most of the iron stains are removed. The skins are then taken out and rinsed in plain water. For book-binding leathers, a mild retanning may be adopted. For other types of leathers, the skins are directly taken for dyeing immediately after they are shaved. The retanning is done in a tub with 1-3% sumac or wattle extract (Kenmosa spray-dried extract) in a float of 150-200% for 15-30 minutes. The skins are then piled to drain.

The dveing in pleated leathers may be done on the retanned skins or on those that have not been retanned. Sometimes a preliminary dye treatment may be given. This treatment is done with 0.25-0.75% acid dyestuffs dissolved in hot water to which 0.25-0.75% formic acid or acetic acid is added. Usually dyestuffs that produce pastel shades only are employed. The skins are dipped in this bath and handled for 5-10 minutes till one gets the required depth of shade. The treated skins are now removed and piled to drain.

# Process No. 1

The excess water present in the skins is first removed by slickering and the skins are placed over a suitable wooden plank (approx. 2' × 2'). Then from the tail-end the skins are pleated so as to form a pattern which is brain-like in appearance. While pleating, one hand is placed over the pleated portion; pleating is done starting from the centre to right side and then centre to left side. This is repeated by adopting a course from side to centre and vice versa. This operation is done according to the convenience of the worker, to attain a brain-shaped surface appearance of the skin. It is better to obtain a close pleating, as close as possible to get a good design. With experience, by modifying the method of pleating the skins, it is possible to produce designs of flowers and leaves. Generally, women workers are found suitable for pleating work. As far as possible the skins must be maintained in a moist condition. If they dry up, the dried portions may be moistened by applying a moist cloth.

0.5-1.0% Dye solution is prepared with suitable basic dyestuffs (preferably slightly darker or stronger than the bottom shade). The required quantity of selected basic dye is mixed with equal quantity of acetic acid and then dissolved in hot water. To this sufficient quantity of cold water is added to make a 0.5-1.0% solution. The dye solution should be poured over the design starting from the centre portion and spread throughout the sides in a circular form covering all the places as far as possible without wasting the dye solution.

The dye solution is poured using a suitable vessel preferably a kettle fitted with a perforated nozzle. A bucket fuil of cold water is kept ready near the working place. A few minutes after pouring the dye solution, the skin is dipped in the cold water as quickly as possible, removed, slickered and nailed on a board to dry in shade. If the nailing facilities are not available, the skin is slickered twice in between, sammed, as practised in E.I. tanning, and allowed to dry completely.

## Process No. 2

The process up to pouring the basic dye solution is exactly the same as in process 1. Instead of pouring the basic dye solution, the same is conveniently sprayed in different angles of the designed portion with the help of a spary gun. The rest of the operations is as in process 1. If the spray equipment is not available then the design is tied with the help of twine thread lengthwise and breadthwise to prevent the falling of the skin. Then the plank is kept in a slant position with a wooden support. The basic dye solution is now poured on the top and allowed to drain through all the portions or in different angles and the draining dye solution collected over a wooden tray. The drained dye solution may be re-used. After a few minutes, the skin is dipped in plain water and worked as described in process 1.

# Process No. 3

In this process the preliminary treatment is done as before. A wooden plank (2' × 2') with a number of perforations is taken. The perforations are at least 1" in diameter and should be as close as possible. The frame is \frac{1}{2}" thick and fixed over a stand. One can also use a suitable wire mesh in place of the perforated wooden frame. The wet skin is spread over the frame grain side up. The skin is now carefully inserted in the perforations with the help of forcfinger till the whole area is covered over the wooden frame. When this operation is completed, the protruding portion under the plank is twisted always in one direction with the help of the hand. When all the inserted portions are twisted, the prepared basic dye solution is poured over the skin starting from the centre and spreading on all sides. This operation is similar to the previous process. The skin is removed after I-2 minutes and worked as in process 1.

Note: By experience one understands how long should be the first and second dye treatments and how the pleating and finishing can be done to get desired designs.

# Process No. 4

In this process one can use E.I. skins directly or give a preliminary dye treatment (to produce a pastel shade) as described in process 1. The skins are well set and dried completely. The dried skins are lightly staked and buffed, if necessary. Then the skins are placed on a table. First a dye solution is prepared with suitable acid dyestuffs to which are added thickening agents like casein, linseed mucilage or

egg albumin to form a solution of reasonable consistency with the dye concentration maintained at 1-3%. A suitable brush (with short, stiff and scattered bristles) is dipped in the thickened dye solution in a shallow basin. The excess dye solution is removed by gently wiping the brush over the sides of the basin. The bristle side of the brush is kept upward and the dye solution is sprinkled over the skins with the help of a stick. This should be done carefully and uniformly throughout the surface of the leather. In this method, more than one dye-stain can be used. In the latter case, it should be taken in the order from lighter to darker stains and the treated skins should be dried after each stain is sprinkled. Then the skins are allowed to dry. When more than one stain is used, the skin may be dried after sprinkling each dye solution. Instead of a brush, a spray gun may be The nozzle of the gun, air pressure and consistency of the dye mixture should be adjusted suitably for the required effect. Lymnato gun can be used for the above purpose as well as for obtaining other attractive designs with the proper use of different nozzles.

#### FINISHING FORMULATIONS

Any one of the following three methods can be used:

Season I: 125 ml. casein (10% solution), 250 g. egg white (8-9 duck eggs approx.), 125 ml. milk (raw), 10 ml. ammonia (liquor). 50 ml. formaldehyde and water to make 4500 ml. The requisite amount of casein is dissolved in a minimum amount of water. One-fourth amount of borax (on weight of casein) is added and well mixed. This borax-casein mixture is heated to get a homogenous solution. Finally the required amount of water is added to get the desired concentration of the casein solution.

The egg white is first mixed in sufficient quantity of cold water; milk and casein solution are then added. Formaldehyde diluted with enough water is added to the former and the solution is made up to 4500 ml.

Season II: 250 ml. milk, 250 g. egg white (8-9 duck eggs approx.), 10 ml. ammonia (liquor) and 50 ml. formaldehyde.: The egg white is first dispersed in a minimum amount of cold water and milk is added to it. Diluted formaldehyde is then added and the season is made up to 4500 ml.

Season III: A-1 part casein (10% solution) and 2 parts water. B-1 part formaldehyde (40%), 2 parts water and liquor ammonia

(few drops). The solution B is added slowly to the solution A by stirring and finally the solution is well mixed. The solution is sprayed on the skins.

To obtain extra gloss, 60-120 g. Neran glaze finish A (ICI) may be suitably incorporated in all the above 3 season recipes, if necessary.

The skins are removed from the nailing board and brushed to remove dust. Then any one of the above seasons is sprayed on the skins; the skins are dried and then glazed. Sometimes, clear lacquer can be used for finishing the treated skins. For this a suitable lacquer (ICI or CLRI top lacquer) is thinned with thinner to the required dilution and sprayed on the skins.

Note: These processes can be applied for all types of E.I. kips and calf skins also, using suitable devices. In such cases, the thickness of the leathers should be about 1.0-1.2 mm.

# SCREEN AND BLOCK PRINTING OF LEATHERS WITH PIGMENTS

R. VENKATACHALAPATHY, K. JAHEER, K. B. GUPTA, D. H. KAMAT, A. C. BASAPPA & K. T. SARKAR

#### INTRODUCTION

The present trend is to produce multi-coloured designs in apparels and in fancy items like ladies' hand bags, wallets, sandals, belts etc. A process has been successfully worked out at C.L.R.I. to convert rejection leathers with pox marks, tick marks etc. from wet blue chrome, E.I. leathers into fancy leathers by screen and block printing into a bewildering variety of designs, to increase their sale value and aesthetic appeal.

#### PRINTING PROCESS BY SCREEN AND BLOCKS

The process is simple and does not require sophisticated equipment and is suitable for adoption in organised sector as well as cottage and medium scale sectors of the leather industry.

#### PERSONNEL

Skilled labour for screen and block printing is available from textile industry which can be advantageously employed by the leather industry after a few days' training.

Screen and blocks of desired designs can be made to order from well established makers of such materials for textile industry.

#### PROCESS KNOW-HOW

C.L.R.I. has developed the know-how of this printing process by standardising the recipe tailored specially for leather, keeping the end uses in view for various leather goods.

#### **EQUIPMENTS**

- (i) Screen printing table
- (ii) Block printing table
- (iii) Screens
- (iv) Blocks
- (v) Steam ager.

Screen printing table for printing 2 pieces of leather and steam ager for steaming 10 pieces of leather at a time have been fabricated at the C.L.R.I. workshop which were used in this demonstration. However the printing table for the steam ager can be fabricated for increased production capacity.

#### RAW MATERIAL

Full chrome crust leathers of either sheep or goat, suede, or grain of inferior quality are used:

#### CHEMICALS

- (1) CLRI printing pigment paste
- (2) CLRI thickening agent for printing
- (3) CLRI fixing agent for printing.

#### PREPARATION OF STOCK THICKENING AGENT

70 g. of thickner is soaked overnight in 930 ml. of water and heated over water bath for 5-6 hours. It is then mixed with other ingredients with the help of a high speed mechanical stirrer. The thickener is then filtered through a filter cloth to avoid lumps. This is important or otherwise the lumps in the thickener will spoil the print as well as the screen. It is advisable to use the thickening agent as fresh as possible for printing.

#### PREPARATION OF PRINTING PASTE

CLRI Printing pigment paste	250 g.
CLRI Thickening agent	700 g.
CLRI Fixing agent	50 g.

250 g. of CLRI printing pigment paste is weighed and mixed thoroughly with 700 g. thickening agent with the help of a high speed mechanical stirrer for 10-15 minutes. 50 g. fixing agent is added to the same mixture and stirred further for 5 minutes, till a paste of required consistency is obtained, for printing with blocks the above paste is thinned with 50 ml. of water.

#### PRINTING PROCEDURE

# Screen printing:

Leathers are fixed on the screen printing table with the grain or suede surface on the top side, as desired, with the help of draw-

ing pins or tingles so that they are well positioned for the registration of designs during the screen printing operation.

Care is taken to remove the wrinkles at the edges of the leathers so as to avoid smudging of the paste on the screen as well as on the leather. Screen No. 1 is now placed on the leather at the 1st registration mark. Sufficient paste is then poured at one end of the screen and drawn down by a soft rubber squeegee with sufficient pressure by two people standing at the opposite ends of the table. Care is taken to draw the paste only upto the leather length to avoid unnecessary wastage of the paste and smudging on the screen. screen is removed without tilting from the leather and kept at the third registration mark and the printing is carried out as described above. Now the screen is placed at the 2nd registration mark and the printing is carried out as usual. This procedure is followed so that the paste on the leather dries out before edges of the screen is placed on it. Similarly printing with differently coloured pastes is done with No. 2 and No. 3 screens. The screens are immediately washed with plain water after the printing is over so that the paste does not dry out in the pores of the screen.

# Printing with blocks:

Leathers to be block printed need not be fixed on the table by pins or tingles but are laid down flat on the table. Printing paste is then poured on the pad. The block is pressed on the pad and then stamped on the leather on the grain or the suede side as desired. The process is repeated taking care to see that registration is achieved over the entire area of the leather. Different pads are used for different colours. A combination of colours of different designs is obtained by using two or more blocks of composite or different designs for printing.

#### DRYING

The above printed leathers are hooked to dry and when dry are taken up for steaming.

#### STEAMING

The dried leathers are kept on the wooden bars and steamed for about 10-15 minutes after closing the lid of the steam ager. The leathers are then hooked up to dry.

#### WASHING

The dried leathers are washed in a tub or a drum with water and non-ionic wetting agent for 15 minutes, and are then washed in plain water twice and hooked up for drying.

#### STAKING

The dried leather is conditioned in saw-dust and then staked lightly in the staking machine or hand staker.

#### DRY DRUMMING

Dry drumming of the above leathers is carried out for 4-5 hours in a clean dry drum for making the leathers soft and to open up the nap in the case of suede leathers. The leathers are then brushed and are measured.

# SCREEN AND BLOCK PRINTED GARMENT LEATHERS FROM WET BLUE CHROME GOAT AND SHEEP SKINS USING DYES

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#### INTRODUCTION:

Today leather is in high fashion as an apparel material. To keep up its image and even improve upon it, newer methods of dyeing and finishing of clothing leathers have been introduced. The screen and block printing of garment leathers is an obvious approach in this direction.

A successful process has been evolved to produce garment leathers printed in a variety of hues and designs. This process can be practised in cottage and organised sector.

Only dyes are used for printing and the dyes are screened for fast to light, perspiration, washing and cleaning.

This technique makes it possible to convert even rejection suedes into high quality fashion leathers that fetch a much higher return. It is believed that these leathers may have a good export market.

#### RAW MATERIAL:

Wet blue chrome goat or sheep skins of 0.7 mm. thickness or above. The skins should contain 2.25-2.5% Cr<sub>2</sub>O<sub>2</sub> on dry weight and possess a shrinkage temperature above 100°C.

For printing on suede side, skins with grain defects may be used and for printing on grain side, skins with defects on the flesh side may be taken. Where crowded designs are printed, skins with defects are also permissible.

#### SHAVING:

Wet blue chrome skins after sammying are shaved on the grain or flesh side depending upon the type of garment leathers to be produced viz. sucde or grain garment leathers, to a uniform thickness. If

the skins are poor in substance then they should be shaved carefully only in the back bone region, in order to level the thickness. As far as possible sheep skins, should not be shaved whether it is on the flesh or grain side, unless they are very thick. Thickness in the sheep skins should be levelled if required by buffing at crust stage or by dry shaving. The shaved weight is noted. The percentage of chemicals to be used for processing are calculated on the shaved weight.

#### **BLEACHING:**

The leathers are bleached in order to bring the stock to a uniform light colour in a drum with the following chemicals:

U.5% Sodium chlorite (Hoechst Dyes & Chemicals)	&	10 Minutes
50% Water		
Add 1% Sodium bi-sulphite + 25% Water	}	30 Minutes
Add 0.3% Oxalic acid	)	
+ 25% water	}	30 Minutes

Drum is flooded with water, run for 10 minutes and drained.

# RECHROMING:

Rechroming is done in the same drum with 6% B & C Chrome poweder (50% Basic) + 30% Water.

The pH of the rechroming bath is adjusted to 3.8, by adding: 0.3-0.5% Soda bicarbonate in 10% water

Drum is run for 20 minutes and bath is drained.

# **RETANNING:**

Retanning is carried out in the same drum with

2% Syntan PN (CLRI)

2% Syntan PC (CLRI)

(pH adjusted to 4.0)

50% Water 35°C

Add 0.2% Oxalic acid

+ 10% Water

The bath is drained and the skins are piled on a wooden horse for overnight.

#### NEUTRALISATION:

Next day the leathers are neutralised with

80% Water.

2% Soda bicarbonate (dissolved in 40% water)

The soda bicarbonate is added in 4 equal instalments at an interval of 15 minutes, finally 0.25% liquor ammonia dissolved in 10% water is added and the drum is run for 15 minutes.

The cut section of leather is checked to PH 6.0—6.2 with Bromocresol purple.

The leathers are washed with 250% water for 10 minutes, drained and rinsed in 250% water at 40°C.

#### **FATLIQUORING:**

The leathers are fatliquored in a drum with

4.5% Lipoderm liquor 2.(BASF India Limited)

4.5% Sandozol K.B.S(SANDOZ India Limited)

0.5% Monogen L.O.C (CHIKA Limited)

0.5% Pine Tar 40 (CAMPHOR & Allied Products Limited)

0.5% Polyethylene glycol 600 (NOCIL)

100% Water @ 55°C.

The drum is run for 45 minutes.

Add 1-2% Formic acid.

15% Water

2 feeds at 10 minutes intervals.

When fatliquor is exhausted, the float is drained and added

1% China Clay

0.5% Maida flour

0.2% White pigment

10% Water

Run for 15 minutes.

Skins are piled on a wooden horse and left over night. Next day they are hooked for drying, conditioned in saw-dust when dry staked, loose toggle dried, trimmed and buffed with 180, 240 and 320 grit emery paper on the flesh side and brushed. For suede garment,

skins are snuffed and buffed, but in the case of grain garment the skins are only buffed to clean flesh side. Goat skins with very rough grain intended for grain garment may be lightly snuffed with used 400 grit emery paper for easy penetration of the printing paste.

Where the printing of the designs is desired on a coloured background, the crust leathers are dyed after wetting back thoroughly. The leathers are dyed into a pastel shade in the normal way. The leathers should be dyed with a light fast, wash fast, penetrative type of acid, direct or premetallised dye. After dyeing leathers are brought into the crust condition and made ready for printing after light staking and loose toggle drying.

# PREPARATION OF PRINTING PASTE:

Acid, direct, and premetallised dyes are used for printing of leathers. All dyes cannot be used for preparing printing paste. Dyes should be screened for light fastness, wash fastness, penetration, tinctorial value, fastness to acid and perspiration resistance. Such of the dyes which satisfy the above requirements should be used for printing purposes.

# PREPARATION OF THICKENER:

Emulsion thickener is prepared using sodium alginate, carboxy methyl cellulose or gum tragacanth powders of medium viscosity.

Gum tragacanth	70 g.
Water	875 ml.
Kerosene	75 ml.
Non-ionic wetting agent— Noigen LS (Chika Ltd.)	50 g.
or Noigen LX 100 (Chika Ltd.)	
or	
Tinoviti-n NR (Suhrid Geigy)	2.4
Preservative (Parachloro meta cresol)	3-4 g.

Gum is sprinkled on the water and mixed with continuous stirring with a stirrer. Next, wetting agent is added to it, followed by kerosene and finally preservative. The whole mass is then stirred for about an hour in an open container with the help of a high speed mechanical stirrer. The pH of the freshly prepared paste is between 6-6.8.

#### PRINTING PASTE FROM ACID & PREMETALLISED DYES:

Dyestuff 40-50 g. Urea 50-60 g. Mixed together Diethylene glycol (NOCIL)

Added:

Water 60°C 250-300 ml. (Mixed together by continuous stirring)

Heated and boiled 1-2 minutes. The solution is cooled and filtered.

To this is added:

Diacetone (NOCIL) 5-10 ml.

This solution is now added to the previously prepared.

Thickener (7%) 450-550 g.

(depending upon the consistency of paste desired) and finally added, just before commencing the printing.

Acetic Acid (glacial) 50 ml.

Water 50 ml.

The printing paste is continuously stirred with a high speed mixer for about 45 minutes to one hour so as to obtain a mixture of uniform consistency.

Note: For deep colours such as blue, red, black and green, the quantity of dyestuff is reduced to 30-40 g. in the printing paste so as to avoid poor fixation of dye. Variety of shades can be obtained by mixing together the pastes of different colours of the same type of dyestuffs in smaller proportions.

#### PRINTING PASTE FROM DIRECT DYESTUFFS

Direct dye 30-40 g. Dye, urea and glycol Urea 50 g. are mixed together Diethylene glycol (NOCIL) 40 g. and then hot water Water 60°C 250-300 ml. is added and mixed well

The solution is heated and boiled for 1-2 minutes, cooled and filtered.

Thickener 450-550 g.
Sodium hydrogen phosphate 15-20 g.
Acetic acid (glacial) 25 ml.
Water 50 ml.

Acid and sodium hydrogen-prosphate are added separately in the paste just before printing, and the paste is mixed well with the help of a mechanical stirrer.

#### FIXING OF SKINS ON THE SCREEN PRINTING TABLE

The leathers are placed flat on the screen printing table. In the case of suede garment leathers, the leathers are placed with suede side up to receive the print impression and vice-versa with grain garment leathers. The leathers are fixed to the wooden printing table by means of drawing board pins, care is taken to avoid folds and wrinkles to prevent smugging. Wooden screen printing table as used in the textile industry for printing work is quite suitable for printing work for printing leathers. Silk screens of standard size usually employed in the textile industry can be used for leather printing. If necessary silk screens to accommodate out-size skins can be specially made and used with advantage.

#### PRINTING PROCEDURE

The silk screen is placed over the leathers on the screen printting table; printing paste is poured into the well of the screen frame and transferred to the leather by drawing it to and fro across the screen with the help of rubber squeege. Generally two passages are given to obtain a clear print on the leather.

To obtain a composite design of three or four colours, leather is each time printed with a silk screen showing the particular part of the design in the screen. Care should be taken to place the peg of the screen well in contact with registration marks (wooden squarcs fixed on the screen printing table for registering the design). As soon as the printing work is over the screens are washed, using a jet of water and drying is carried out by wiping out with an absorbent cloth and keeping them in warm place. Too much heat will warp a screen frame. Screens should not be left to dry with paste as otherwise they will prove difficult to clean. It may also lead to blocking of the screen mesh.

#### **BLOCK PRINTING**

For block printing a flat wooden table covered with a suitable cushiosing material is used. Leather is placed flat on the table and printing is commenced from the butt and belly regions, to the middle and neck regions of the leather.

The wooden block engraved with the design is first placed over the wooden tray (similar to one used in textile industry) in which printing paste has been already poured on the absorbent pad and made uniform with the help of a brush. The block is lightly pressed on the pad to pick up the paste and then is placed on the leather and struck by hand or a wooden mallet to effect even and thorough penetration of the paste. A separate block is used for each one of different colours that go to make the composite design. Blocks are washed after use and kept in a warm place to dry.

#### **CURING & FIXING OF PRINT**

After the leathers have been printed, they are carefully removed from the table, dried for a few hours and then subjected to steam treatment for 8-10 minutes (First steamed for 3-4 minutes, cooled and resteamed for 3-4 minutes) in a suitable steamer. The steaming operation is carried out at or only very slightly above atmospheric pressures at temperature around 100°C. This treatment is given to fix the colour. Care should be taken to avoid shrinking of leathers due to over steaming.

For improving fixation of the dye, the steaming can be repeated 3-4 times with steaming for 2-3 minutes only each time.

The steamed leathers are dried for about an hour and further treated in a tub with

300-400% Water-35°C

½-1% Formic Acid (adjusted to pH 4)

½-1% Cationic Dye Fixative (Amigen L) (Chika Ltd.)

OF

Derma-fix (Sandoz India Ltd.)

or

Tinofix (Suhrid Geigy Ltd.)

for 10-15 minutes

and made shower proof if necessary by treating in the same bath with 2-3% chrome stearatochloride for 15 minutes.

The leathers are finally washed thoroughly in running water in a tub. Leathers are hooked up for drying, when dry, conditioned in saw dust, lightly staked, dry drummed for 1-2 hours, loosely toggle dried, trimmed, area measured and brushed.

In addition to the manufacture of garments these leathers can also be used for manufacture of fancy leather goods and other novelty articles.

# J. K. KHANNA, P. S. VENKATACHALAM & T. S. KRISHNAN

#### **ENTRODUCTION**

Tie and dye leathers are generally made from wet blue sheep and goat skins and are very popular. Such leathers are being made by a few tanning units in India and are exported. Many attempts were made to produce these leathers from E.I. skins but were not successful due to the fact that bright shades were difficult to achieve in tub dyeing.

There are however many advantages in making these leathers from E.I. skins. It is easier to select the pieces in E.I. stage. The leathers have better fullness, nap and handle. The disadvantages are less bright colours and poor dry rub resistance. With proper selection of dyes and dye fixatives it has been found possible to achieve fairly bright shades with a reasonable degree of rub resistance.

#### RAW MATERIALS

E.I. sheep and goat skins free from major flesh side defects having an area of not less than 64 sq.ft. per bond of dozen skins are preferred. Skins should not be unduly thick in neck and backbone regions. E.I. sheep skins of  $6\frac{1}{2}$ -7 lb. and E.I. goat skins of  $8\frac{1}{2}$ -9 lb. per bond of 12 skins are ideal weight ranges for such leathers. The skins are weighed and trimmed.

# WASHING, STRIPPING AND WASHING

The skins are washed in drum for 15 minutes with 600% water after which stripping is done for 45 minutes using 400% water, 0.5% Idet 10 (Swastik Co. Ltd.) and 2% borax. Borax is dissolved in water (10% solution) and added in 2 feeds at an interval of 15 minutes. The stripped skins are washed for 10 minutes with 600% water.

#### SOURING AND CHROME TANNING

The washed skins are soured in a drum for 30 minutes with 0.25% oxalic acid, 0.25% formic acid (85%) and 400% water. The pH of bath at the end of souring should be 3.6 to 4.

# PREPARATION OF CHROME LIQUOR

10% chrome extract powder (24-25% Cr<sub>2</sub>O<sub>3</sub>) is dissolved in hot water the previous day to give chrome liquor of about 33½% basicity. After cooling, the chrome liquor is divided into three portions and two portions are basified to 40% and 50% levels respectively by adding the requisite amount of soda ash. The soda ash is dissolved in water (10% solution) and added slowly to the portions of cooled chrome liquor stirring well all the time. The chrome liquors are left to age overnight.

# RETANNING WITH CHROME

To the souring bath, a portion of chrome liquor (33½% basicity) is added and the durm is run for 30 minutes. The second portion of chrome liquor (40% basic) is added and after running for 30 minutes, chrome liquor (50% basicity) is added and the skins are further drummed for ½ hours after which 2 to 2.5% soda bicarb. dissolved in water (10% solution) is added in 5 or 6 feeds at intervals of 15 minutes. The goods are finally run for 1 to ½ hours and the pH of bath is checked. It should be about 4. The shrinkage temperature of the leathers should be not less than 100°C. 300% water is added to the drum and after running for 10 minutes, the bath is drained. The skins are horsed up overnight.

## NEUTRALISING

The skins are washed in a drum with 600% water for 15 minutes. They are then neutralised with 0.5% sodium formate and 1.25 to 1.5% soda bicarb, and 400% water. Formate which is dissolved in water is added first and after running for 15′ the soda bicarb which is dissolved in water as 10% solution is added in 3 feeds at intervals of 10 minutes. The goods are finally run for 30′ or more, till the pH of cut section is throughout 5.5. The cut edge when tested with bromo crosol green indicator should react blue throughout. The neutralised skins are washed with 600% water at 45°C for 10 minutes and again for 10 minutes with 600% water at 55°C.

# **FATLIQUORING**

The washed skins are floated in a bath of 200% water at 55°C and fatliquor consisting of 7.5% sulphonated groundnut oil (9 to 10% in the case of goat skins) which is emulsified with hot water is added and the drum is run for 45 minutes. If necessary to exhaust the bath, 0.25 to 0.5% acetic acid which is diluted with water is added in 2 or 3 feeds at intervals of 5 minutes. The goods are finally run for 10 to 15 minutes after which the bath is checked for exhaustion. The bath is drained and the goods are horsed up overnight.

The leathers are set on the flesh side in machine and are hooked for drying in a cool place. When dry, they are taken out, crusted for a few days, saw-dusted overnight, staked well and air dried. The dried skins are trimmed and buffed on flesh side with 240, 320 and 400 grit papers. In the case of thick skins, they are buffed on grain side with coarse emery paper. After brushing well, they are assorted for proper buffing and weighed.

#### TIE DYEING

# (a) BASE DYEING

# Wetting

The weighed skins are floated in a drum containing 800% water at 55°C to which 1% ammonia (0.88) and 1% Teepol B 300 (shell) are added. After running for 1 to 1½ hours, the skins are left overnight in the bath. Next day the drum is run for 20 minutes after which they are checked for proper wetting. The bath is drained and the leathers are washed twice with 600% water at 45°C & 55°C respectively, the duration being 10 minutes for each wash. The skins are again floated in a fresh bath of 400% water at 55°C to which 0.75% ammonia is added. After running for 10 minutes 4% Chlorazol Orange PO Conc. (ICI) which is dissolved in hot water (1:40) and filtered is added in two feeds at intervals of 10 minutes. The goods are run for 1 to 14 hours after final addition. 2 to 2.5% acid formic (85%) which is diluted with water (1:10) is added in 4 or 5 feeds at intervals of 5 minutes. The drum is run finally for 20 to 30 minutes and the dye bath is checked for exhaustion. The bath is drained and the goods are briefly rinsed in 800% water to which 0.1 to 0.2% formic acid is added. The bath is drained.

The skins are now marked on the grain side for suitable design and tied. They are dyed with 1% Chrome Leather Brown BRLL (CIBA) in a tub containing 400% water at 50 to 55°C. After handling for 15 to 20 minutes, the bath is exhausted by adding 1% formic acid (85%) diluted with 10% water in 2 or 3 feeds at intervals of 5 minutes. The skins are further handled for 10 to 15 minutes till the dye bath is exhausted. They are washed once or twice in acidified water to remove any loose dye and they are finally entered in a fixing bath consisting of 400% water, 0.5-0.75% formic acid and 0.5% Amigen L (Chika Ltd.). After handling for 15 minutes, the bath is drained. The skins are taken out and the threads are opened. The skins are finally handled in a bath containing 0.5% formic, acid 0.5% Amigen I. and 3% chrome stearato chloride and 300-400% water at 45°C for 15 minutes.

After draining the bath, the leathers are rinsed in water, squeezed and hooked to dry. The dried skins are saw-dusted for a few hours, staked in pairs, dry drummed till the nap is opened up well and are finally toggle-dried. They are then removed, trimmed if necessary and brushed.

# PARCHMENT FROM HIDES AND SKINS FOR USE IN ORTHOPAEDIC APPLIANCES, MUSICAL INSTRUMENTS, PUPPETS AND SPORTS GOODS

R. SELVARANGAN,
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Parchment used in musical instruments, puppets, orthopaedic appliances and the like is at present manufactured by the chamar by traditional methods. Fresh hides and skins are pegged to the ground and dried in the sun, keeping the grain side up. Ash is strewn on the grain side and when they are semi-dry, the hair is scraped off and the pelts so obtained are used as such for drums and straps for musical instruments. In certain other cases, fresh goatskins are left in lime liquor for a few days, unhaired, fleshed, worked to uniform thickness and dried. In yet another process, buffalo calf skins are soaked in water for a few days and worked on every day till the hair and flesh which are loosened by bacteria are removed by knife. Next. the pelts are thinned uniformly with a knife. The transparent parchment thus made will be crude in appearance and is liable to putrefaction and destruction by insects; also the process of soaking may lead to dissolution of much of the valuable hide substance, resulting in holes in the pelt.

Improved methods have been developed for manufacture of transparent and opaque parchment from raw hides and skins to suit the conditions of both modern and small scale tanners. The processes involve one of the following: (i) splitting of heavy hides and drying the layers; (ii) enzymatic unhairing, fleshing and drying; (iii) straight liming, unhairing, fleshing and bringing the pelt to the isoelectric point and drying and; (iv) stiffening of parchment by chemical treatment.

# I. RAW PARCHMENT

Wet salted buffalo hides are soaked in water overnight. Next day, they are green fleshed, washed three times and split into grain, flesh and middle layers. The grain and flesh layers are taken for limed parchment. The middle layers are washed thoroughly, weighed and treated with 2.5% borax in 200% float of water with addition of 0.1% p-chloro-m-cresol, proper handling or drumming being carried out for 1 to 2 hours. The pieces are then toggled on drying frames and allowed to dry for two days. The dried pieces are transparent and 1 mm. thick.

Some pieces are treated with 1.5% formaldehyde instead of borax and p-chloro-m-cresol, and dried as before. The dried pieces are opaque, white, and 0.6 mm. thick. This process is also applicable to cow hides, goat and sheep skins. However, uniformity and clarity of the parchment prepared from cow and sheep are not good when compared with those from buffalo and goat respectively.

#### II. ENZYME TREATED PARCHMENT

Wet salted goat skins are soaked in water for 30 minutes and given three changes of water to remove dirt, salt etc. and weighed. Skins are left in 300% water containing 2% madar (Calotropis gigantea) liquor and 5% salt and handled twice during a period of 24 hours. They are washed with water, unhaired, fleshed and treated with 0.1% p-chloro-m-cresol in 200% float for 30 minutes and then taken for toggling and drying. The skins are then scraped with blunt knife or buffed to get an opaque parchment of 0.4 mm. thickness. The process is also applicable to hides.

## III LIMED PARCHMENT (TRANSPARENT)

Wet salted buffalo hides are cut into sides, soaked in water overnight and given three changes of water next day. They are then green fleshed, weighed and taken for liming.

The sides are limed with 30% slaked lime and 400% water on the soaked weight and handled twice daily for 8 days. On the 9th day they are unhaired, fleshed, washed and then split into 2-3 layers, washed, drained and weighed.

The sides are now delimed with 2.5% formic acid and 300% water on the pelt weight with addition of 0.1% p-chloro-m-cresol. Formic acid is diluted with water and given in six equal instalments at intervals of 20 minutes. After the last addition, the sides are handled further for one hour and left in the same bath overnight. Next day, they are handled for one hour in the same bath and taken for drying. The pH of the pelt is found to be about 4.5. The sides are toggle-dried for 2 days.

This process gives a stiff and transparent parchment. (The thickness of the grain and middle layers was 1 mm.) The grain and the flesh layers of the raw parchment may also be processed in this manner. (The thickness of the grain parchment in this case was 0.5 mm. and flesh layer 1 mm). However, the thickness of the raw grain splits was not uniform.

This process is also applicable for making transparent limed goat skin parchment. In this case, the number of days of liming is reduced to 6 days. Goat parchment is highly and uniformly transparent and of thickness 0.3-0.5 mm.

Goatskin parchment produced by deliming with 1% ammonium chloride and 0.1% p-chloro-m-cresol is found to be stiff. However, the transparency of this parchment is uniform. This process is also applicable for other kinds of hides and skins.

# IIIb. LIMED PARCHMENT (OPAQUE)

Limed hides and skins after unhairing, fleshing and washing are delimed with 1% ammonium chloride and 200% water (on the pelt weight) for 30 minutes, treated with 3% borax, 0.1% p-chloro-m-cresol and 200% water for 30 minutes to one hour and left overnight in the same bath. Next day, they are handled again for 30 minutes and taken for toggling and drying. The dried parchment is lightly buffed with fine grade emery paper to get uniform opaqueness. The thickness of the grain and middle layers of a hide is about 0.8 to 1 mm. and that of goat skin 0.2 mm.

#### IV. STIFFENED TYPE PARCHMENT

The parchments prepared from hides and skins after liming and deliming with ammonium chloride are chemically treated for stiffness. The chemicals used are tanning agents like basic alum, chrome or formaldehyde. These are used in minimum quantity just to stiffen the parchment without undue tanning.

The delimed pieces are treated with 1% basic aluminium sulphate (0.25% Al<sub>2</sub>O<sub>3</sub>) or 1% chrome extract (0.25% Cr<sub>2</sub>O<sub>3</sub>) or 1% formal-dehyde and 1% borax in 200% float (all on the pelt weight) for 1-2 hours, rinsed with water, treated with 0.1% p-chloro-m-cresol and taken for toggling and drying. The parchments from goat skins (aluminium sulphate treated) are 0.1-0.3 mm., chrome treated—0.3 to 0.5 mm. and formaldehyde-borax treated—0.7 to 0.9 mm. in thickness. This process can also be applied to other kinds of hides and always.

Thus the processes given above for the manufacture of parchmen from hides and skins yield products varying in thickness, transparency and stiffness to suit the intended uses viz., making membranes and straps for musical instruments, base for puppet cuttings, linings in orthopaedic appliances, sports goods etc. and carved window panels attached to the glass doors, lamp shades, light weight boxes, fancy articles etc.

S. BANGARUSWAMY

#### INTRODUCTION

Wool sheep skins are often dressed into footings or cheap fur linings for boots, gloves and leather garments. The Rajasthan and Kashmin skins and to a lesser extent skins from the Mysore area find use for such purposes. Here is a process for dressing and dyeing such material.

#### RAW MATERIAL

Wet salted Kashmir wool sheep skins.

1:15

#### SOAKING

Salt—10 gm/l.

Teepol B-300 (M/s. NOCIL)—10 gm/l.

Saginol T liquid (M/s. Rishi Roop Chem. Co.)—0.25 gm/l.

Time-2 hours.

Paddle 5': Rest 10'.

#### SCOURING

Soda ash-1 gm/l.

Teepol B-300-1 gm/l.

Sodium lauryl sulphate—1 gm/l.

Time-2 hours.

Temperature-38°C.

Paddle 5'; Rest 10'.

(Higher amounts of chemicals, longer duration of scouring and 3-5 gm/l of mineral turpentine besides the above chemicals may be employed for skins with excessive grease).

#### WASHING

Warm water (38°C)-5'.

#### FLESHING

Machine/hand.

#### WASHING

Warm water (38°C)-5'.

#### **PICKLING**

Salt-60 gm/l.

Sulphuric acid (98%)-3 gm/l.

Time-40 hours.

#### TANNING

(A) Basic aluminium sulphate 'plus' Basic chromium sulphate Salt-50 gm/l.

mixed — given in 3 instalments of 15' interval.

Cr<sub>s</sub>O<sub>s</sub> (basicity 33%)
1.0 gm/l.

Paddle 5': Rest 10'.

Time-24 hours.

(penetration: complete).

#### BASIFICATION

Sod. bicarbonate—0.25.—0.5 gm/1.

+

Sod. acetate -0.25 -0.5 gm/1.

Paddle 5'; Rest 10'.

Repeat the process to pH 3.8 of the bath.

Paddle 1 hour at pH 3.8.

#### PILING

Flesh to flesh (minimum overnight).

(B) Basic aluminium sulphate

Same as (A) excepting that 1.8 gm/l of Al<sub>2</sub>O<sub>2</sub> (basicity: 33%) used in the place of mixture of Al + Cr.

Fancy—14

The rest of the unit processes detailed below are the same for (A) and (B) and are carried out separately.

#### Washing

Warm water (40°C)-5'.

#### Neutralisation

Salt-20 gm/l.

Sod. bicarbonate—1 gm/l.

Temperature 40°C.

Paddle 5'; Rest 10'; repeat the process to pH 6.5 of cut section: purple to Bromocresol purple.

#### Washing

Warm water (40°C)—5'. Piled to drain/centrifuge/samm.

## Oiling .

Lipoderm liquor II (M/s. BASF)—1 part + Water (60°C)—2 parts The emulsion is applied on the flesh side.

# Piling

Flesh to flesh overnight.

# Drying

Hooked to dry.

# Post-tanning operations

Drummed with moist sawdust, (caging in a caging drum preferable at this stage) staked, drummed with sawdust containing mineral turpentine (3% on the weight of sawdust) for 30 minutes (caging preferable), staked again, if necessary and the flesh side buffed on the over-shot wheel—carding and shearing are done at this stage.

# Bleaching

Float 1:30.

Sod. hydrosulphite—5 gm/l.

Soda ash-0.5 gm/l.

Triton X-100 (Rohm & Hass)—0.5 gm/l.

Temperature—40°C.

Time—2 hours.

To the same bath is then added formic acid 1 gm/1.

Time—overnight.

The skins are washed thoroughly and Leucophor WSI liquid (M/s. Sandoz) 0.1 gm/l. added to the final wash-bath and kept for 15'. The skins are then taken out, oiled on the fish side with 1:4 emulsion of Lipoderm liquor II in water and hung to dry. The skins are then staked. Carding, shearing and ironing are done at this stage.

### Dyeing

- (A) Busic aluminium sulphate plus basic chromium sulphate—tanned skins.
- (i) Dyeing with Navicet Pink RF (M/s. BASF):

Float--1:25.

# (a) Killing:

Soda ash-1 gm/l.

Sod. lauryl sulphate—1 gm/l.

Triton X-100-1 gm/l.

Temperature-35°C

Time--1 hour.

The skins are then rinsed thoroughly and sammed.

# (b) *1) yeing*:

Navicet Pink RF-3 gm/l.

Pasted with Triton X-100—1.5 gm/l and water (70°C)—15 gm/l added, stirred well and the whole thing added to the dye-bath (50°C).

Dyeing time-1 hour.

The dyed skins are rinsed thoroughly (clear wash-water) and hung to dry. The skins are then sawdust-drummed till the superfluous colouring matter is removed, (caged) and staked, Carding, shearing and ironing are done at this stage.

- (ii) Dyeing with Ecarlate Dimacide Lumiere R (M/s. Francolor):
  - (a) Killing:

As for (i) above.

(b) Dyeing:

Ecarlate Dimacide Lumiere R-1 gm/l.

Acetic acid—2 gm/l.

Salt—5 gm/l.

Time-30'.

Temperature-60°C.

To the same bath is then added,

Formic acid—1 gm/l.

Time-30'.

Temperature—60°C.

The dyed skins are then rinsed thoroughly (clear wash-water) and the process followed as far (i) above.

- (B) Basic aluminium sulphate-tanned skins: Dyeing with oxidation type of dye:
  - (a) Killing:

As in A (i) above.

(b) Mordanting:

Sodium dichromate crystals—1 gm/l.

Acetic acid—0.5 gm/l.

Time-overnight.

## (c) Dyeing:

Nako Brown 3 G (M/s. Hoechst)—1 gm./1.

Liquor ammonia—1 ml.

Hydrogen peroxide (20 vols.)—2.5 ml/l.

The mordanted skins are placed in the above dye bath and handled for 1 hour. To the same bath is then added hydrogen peorxide (20 vols.) 2.5 ml/l.

Dyeing continued for further 5 hours. The skins are then taken out, washed thoroughly (clear wash-water), piled to drain, oiled on the flesh side with 1:4 emulsion of Lipoderm liquor II and hung to dry.

Drumming with sawdust and other mechanical operations are done as for A (i) above.

## Preparation of basic aluminium sulphate liquor

Aluminium sulphate (Al<sub>1</sub>(SO<sub>2</sub>)<sub>2</sub>. 18 H<sub>2</sub>O) powder—10 kg. Water—10 litres, stirred and left overnight.

To the same is then added sodium citrate—700 gm. followed by soda ash—1.75 kg. in water—20 litres, while stirring.

(The liquor will have about 40 gm Al<sub>2</sub>O<sub>2</sub>/litre and 33% basicity).

R. SELVARANGAN, R. V. SOVANI &

Y. Nayudamma

Leather is a versatile substance serving many needs; one of its uses is in the manufacture of toys. The leather used should be flexible and lend itself to colouring and painting making it an ideal covering for the toys with the necessary strength, suppleness and resistance to micro-organisms and pests. The toys prepared should also be unbreakable. In several countrier like India, there is a good trade in leather toys. Though the necessary skill in toy making is available, the leathers used are not of good quality. Work has been conducted to meet this need and the following process has been found to yield satisfactory leather.

#### **RAW MATERIALS**

100 wet salted still-born kid skins 40-50 cm. (16-20") in length are taken.

#### SOAKING

The skins are soaked in a bath consisting of 400% water, 15% salt, 0.25% zinc chloride, 0.1% sodium trichlorophenate for 2 hours. They are then washed in 3 changes of water (400%) for 10 minutes each.

They are next green fleshed with a kurpi to remove adipose tissue-

#### PICKLING

The skins are then pickled in an acid-salt mixture consisting of 1.5% sulphuric acid, 10% common salt and 100% water (on the soaked weight). The pieces are handled in the pickle bath, beamed during pickling and made soft by the help of rapi (a special slicker) about four times and left in the pickle for a total period of 2 days.

#### **TANNING**

The goods are then tanned in a blended tanliquor prepared by using 1.5% B & C chrome extract, 2.0% aluminium sulphate, 1.0% sodium citrate and 3.0% formaldehyde (on the soaked weight). The materials are dissolved separately. The solutions of aluminium

sulphate and sodium citrate are first mixed and the chrome extract solution is then added to it. At the end, formaldehyde is added to the mixture.

Half of the pickle liquor is drained out and the skins are placed in the remaining pickle bath. The tan liquor is added in four instalments. The skins are left in the bath, being handled twice in a day. Next day, 10% soda ash solution is prepared and a quantity of this solution containing about 0.5% soda ash on the soaked weight is added slowly in three instalments in the course of the day—the skins being handled—to raise the pH of the liquor to around 4.2. The goods are kept for one more day in the bath being handled twice during this period. Next day, they are washed first with water and then with 1% solution of Noigen LS (Chika Ltd.), for about 10 minutes and finally again washed with water.

## **FATLIQUORING**

The warhed skins are fatliquored using 3-4% of Cation Liquor O(BASF) and 2% french chalk. First the oil is applied on the flesh side of the skin; the skins are piled flesh to flesh and kept for 2 hours. Then the french chalk is rubbed uniformly on the flesh side and the skins are hung up for drying. During drying, the skins are staked thrice. When dry, they are buffed on the flesh side and trimmed. The hair side is cleaned with a soft brush. The skins are now ready for making toys.

#### S. BANGARUSWAMY & A. SALLAM

Dik-diks are found living in burrows under the trees and shrubs almost throughout Somalia. They are herbivorous in their eating habit. These animals are hunted both for their meat and skin and are caught by trapping. The skin of a mature animal measures about 1½ sq. ft. The skins are preserved by drying and it is reported that as many as 500,000 skins are exported to other countries in this raw, dried condition. A certain number of skins are processed within the country and the processed skins are made use of in the fabrication of rugs, ladies' hand-bags, sandals, etc. The processing of dik-dik skins, as practised in Somalia at present, consists of soaking, fleshing by hand-knife, alum-pickling, chrome tanning in tubs and straightaway oiling off on the flesh side of the skins with neutral oils, e.g. sesame oil.

The United Nations Special Fund Programme operating at present in Somalia have proposed, among other measures for the improvement and better utilisation of hides, skins, leather, etc, of the country, that these dik-dik skins could be dressed as furs by modern technological methods within the country and exported to earn more foreign exchange besides fetching better returns within the country. As a part of their development programme, one of the authors of this article arranged to bring the skins of dik-dik to the Central Leather Research Institute, Madras and after a series of trials at the Pilot Tannery of the Institute, a process was developed. The process is given in detail.

## Dressing

Raw material: Dried dik-dik skins.

Float: 1:30 (for bigger lots, this could be 1:25).

1st day: Soaking:

Salt : 10 g./l.

Triton X-100

(Rohm & Haas) : 1 g./l.
Sodium trichlorophenate : 0.1 g./l.

Duration overnight

## 2nd day:

The following day (after 24 hours' soak), the skins are fleshed in a fleshing machine and then resoaked in a fresh bath. Added to the same bath,

 Salt
 : 10 g./l.

 Triton X-100
 : 0.5 g./l.

 Sodium lauryl sulphate
 : 0.5 g./l.

 Sodium trichilorophenate
 : 0.1 g./l.

Duration overnight

3rd day: Scouring: (for greasy skins).

 Soda ash
 : 0.5 g./l.

 Triton X-100
 : 0.5 g./l.

 Sodium lauryl sulphate
 : 0.5 g./l.

 Temperature of the bath
 : 38°C

Duration 1 hour (paddle)

The skins are then washed with warm water (38°C) in the paddle for 10 minutes. At this stage, refleshing may also be done, if necessary.

# Pickling:

Salt : 60 g./l.

Formic acid (85%) : 3 g./l.

Sulphuric acid (98%) : 1 g./l.

The skins are paddled for 1 hour and pickled for about 40 hours.

4th day: The paddle is run for 1 hour.

5th day: The paddle is run for 10 minutes. The skins are then taken out and horsed up for thorough draining.

# Tanning:

Salt : 50 g./l. Lipoderm liquor II : 3 g./l.

M/s. (BASF)

Formaldehyde (40%) : 3 ml./1.

Fancy-15

Temperature of the bath : 35°C

Duration 2 hours (paddle)

Added to the same bath,

Sodium bicarbonate : 1.5 g./l.

Duration 2 hours (paddle)

Added to the same bath,

Basic aluminium sulphate liquor : 1.8 g. Al<sub>3</sub>O<sub>3</sub>/l. (citrate-masked) (33% basicity)

Duration 2 hours (paddle) and left overnight in the liquor.

## 6th day

The paddle is run in total for 24 hours after the addition of basic aluminium sulphate. The skins are then horsed up to drain well and piled flesh-side-up on a table.

# Oiling

The flesh sides of the skins are then oiled by hand/brush with an emulsion of 1 part of Lipoderm liquor II (BASF) in 2 parts of water and left in pile overnight flesh to flesh.

# 7th day

· The skins are hung to dry.

# Post-tanning Mechanical Operations

The dried skins are drummed with moist sawdust for 30 minutes, hand-staked, aired-off, drummed with saw-dust containing mineral turpentine (2-3% on the weight of saw-dust) for 1 hour, caged, staked again and the flesh side buffed on the overshot wheel.

# Dyeing

1st day: Scouring

Soda ash : 1 g./l.
Triton X-100 : 1 g./l.
Sodium lauryl sulphate : 1 g./l.

Temperature of the bath

Duration 2 hours

: 38°C

The skins are then rinsed well, first with warm water (38°C) followed by water at room temperature.

# Mordanting:

Ferrous sulphate (crystalline) : 8 g./l.

Potassium hydrogen tartrate : 1.5 g./l.

Salt : 30 g./l.

Triton X-100 : 0.5 g./l.

The skins are paddled for 2 hours and left overnight in the bath.

## 2nd day: Bleaching

The following day, the paddle is run for 30 minutes and the skins are entered into a bleach-bath whose pH had been adjusted to 8 by the addition of ammonia.

Hydrogen peroxide (20 volumes) : 40 ml./l.
Salt : 50 g./l.
Sodium lauryl sulphate : 0.5 g./l.

(\*The amount of hydrogen peroxide may be increased for the bleaching of skins with highly pigmented matter).

The paddle is run during the day and the addition of hydrogen peroxide is made in two equal instalments with an hour's interval between each addition. The skins are left in the bath overnight. Throughout the process of bleaching, the pH of the bath is maintained at 8.0.

# 3rd day

The paddle is run for 1 hour. The skins are then entered into a bath containing oxalic acid: 1 g./l. and salt 30 g./l. and paddled in this liquor for 2 hours.

The skins are washed thoroughly in water and mordanted.

```
Mordanting: (Dyeing grey)
Sodium dichromate
                              x g./l. (e.g 1 g./l.)
    crystals
Acetic acid
                              \frac{1}{2} x g./l. (0.5 g./l.)
Duration overnight
Dyeing:
Nako Grey BK
Hoechst, for the desired depth of shade
                               y g./l. (eg. 1 g./l.)
Hydrogen peroxide
(20 volumes) in 3 in-
stalments (30 minu-
tes' interval)
pH of the bath
                          : 9 (adjustment with ammonia)
Total duration 6-7 hours
```

The skins are then washed thoroughly with water, scoured with sodium lauryl sulphate: 1 g./1. and Basyntan FCBJ (BASF) (or CLRI syntan NC) 1 g./l. for 30 minutes at 35°C, washed with water, horsed up to drain, oiled as before and hung to dry. The dried skins are drummed with saw dust for 1 hour (or till the superfluous colouring matter is removed) and staked. After caging, the skins are ready for grading.

The processes of dressing bath/brush tanning with basic aluminium sulphate/basic aluminium sulphate+basic chromium sulphate/zirconium tanning salts and dyeing of rabbit skins are described in detail.

Rabbit skins are one among the abundantly available fur materials. They are characterised by their silky fur and the pelts are thin in substance and light in weight; dressed/dyed rabbit skins find extensive use in the manufacture of articles, for warmth and adornment; these articles, many of them fashionable indeed-hats, fur garments, gloves, ladies' hand bags, novelty jewellery cases etc., are made partly and mainly of these skins. The dressing of rabbit skins is done on a cottage scale, mostly in the Kashmir valley and the quality of the finished product is not quite satisfactory. The dressed skins are often papery, assume damp feel during rainy season and the 'preservation' given to them is not fast to washing and the articles made from these skins do not appeal favourably to the consumers. The processes of dressing and dyeing developed after the research work at the Central Leather Research Institute are given here for the benefit of the fur dressers and it is hoped that better quality skins and hence better quality articles would be produced which would satisfy the consumers and earn greater volume of foreign exchange through exports.

#### DRESSING

Raw material

Dried white rabbit skins.

1st day: Weigh the raw material (W.kg.). Employ the float at 25 × W litres for all the unit processes.

#### SOAKING

Salt (sodium chloride)—10 g./l.
Triton X-100 (Rohm & Haas)—1 g./l.
Sodium trichlorophenate
(Ahura Chemicals)—0.1 g./l.
Soda ash—0.25 g./l.
Duration overnight.

2nd day: The skins are fleshed and taken for scouring.

## SCOURING (for greasy skins)

Soda ash-0.5 g./l.

Triton X-100-0.5 g./l.

Sodium lauryl sulphate

(Ahura Chemicals) 0.5 g./l.

Duration 2 hours (Paddle/handling-wooden stirrers could be used).

Temperature-38°C.

Wash with warm water (38°C).

#### PICKI ING

Salt-60 g./l.

Sulphuric acid (98°)-2.5 g/l.

Duration-40 hours.

3rd day: Move the skins in the pickle bath.

4th day: Take out the skins from the pickle bath. Allow to drain thoroughly (at least for 1 hour).

#### **TANNING**

Tanning can be done either in bath (paddle/handling) or by brushing.

#### A Rath

(Paddle/handling - wooden stirrers could be used).

Salt-50 g./1.

Lipoderm liquor II (BASF)-3 g./l.

Formaldehyde (40%)-3 ml./1.

Duration 2 hours.

#### Add to the same bath-

Sodium bicarbonate 1.5 g./l.

dissolved in Water-15 ml./l.

Duration 2 hours.

Add to the same bath

Basic aluminium sulphate liquor (33% Basicity) 1.8 g. Al, O,/1.

or

Basic aluminium sulphate (33% Basicity) 0.8 g. Al<sub>2</sub> Q<sub>3</sub>/1. (Plus) Basic chromium sulphate (33% Basicity)—1.0 g. Cr<sub>2</sub>O<sub>3</sub>/1. Duration 24 hours.

- 5th day: Take out the skins. Allow to drain well (at least for 1 hour). Take for oiling.
- B. Brushing (Brush/hand—application) Method I (Aluminium tanning salt)

#### 4th day: 1st coat:

Basic aluminium sulphate liquor—1 part.

(Plus) water-

2 parts.

Salt-50 g./l. of the above diluted liquor.

Leave on pole, flesh side outwards.

Duration 5 hours.

(Polythene sheet may be used to cover the skins).

## 2nd coat:

Basic aluminium sulphate liquor-As such.

Salt-50 g./l. of the aluminium sulphate liquor taken.

Leave on pole as before.

Duration overnight.

#### 5th day

3rd coat: (preferable).

Basic aluminium sulphate liquor-As such.

Salt-50 g./l. of the aluminium sulphate liquor taken.

Leave on pole as before.

Duration 6 hours. Take for oiling.

# Method II (Zirconium tanning salt)

4th day: 1st coat

Tanning salt ZR. M/s Kohinoor

Engineering Co., Madras) : 100 g./1.

Salt : 50 g./l.

Water to make : 1 litre.

Leave on pole, flesh side outwards.

Duration 5 hours.

2nd coat: Composition—As for the 1st coat.

Duration overnight.

5th day:

3rd coat: Composition—As for the 1st coat.

Duration 6 hours. Take for oiling.

# OILING (Bath/Brushing):

5th day: Add slowly

Lipoderm liquor II—1 part to 2 parts of hot water with stirring. Allow the emulsion to cool. Application—Brush/hand. Leave in pile flesh to flesh, overnight.

6th day: Hang to dry.

#### POST-TANNING MECHANICAL OPERATIONS

Drum the dried skins with moist saw dust for 30 minutes. Cage. Handstake.

Drum with saw dust containing mineral turpentine (2%-3% on the weight, of saw dust) for 1 hour, if found greasy. Cage. Stake again.

Buff the flesh side on the over-shot buffing wheel.

The skins are now ready for bleaching/dyeing.

#### BLEACHING

(This is not absolutely necessary if the skins are taken for dyeing).

Soda ash-0.5 g./l.

Sodium hydrosulphite-3 g./l.

Triton X-100-0.5 g./1.

Duration 2 hours.

Temperature 35°C

Add to the same bath

Sulphuric acid (98%)-0.25 g./l. in

Water-5 ml./1.

Duration 5 hours.

Take out the skins. Wash well.

Add Leucophor WSI liquid (Sandoz)—0.1 g./1. to the final wash water; handle the skins for 10-15 minutes.

Take out the skins. Allow to drain and apply oil emulsion as above, if necessary. Hang to dry. Hand stake and grade the skins.

Dyeing of dressed rabbit skins (Tannage, using a material other than chrome)

(Bluish black)

Method 1-1st day: Killing

Soda ash-3 g./l.

Liquor ammonia—3 ml./l.

Triton X-100-0.5 g./l.

Duration 2 hours.

Wash the skins thoroughly. Allow to drain well.

# Mordanting.

Sodium dichromate crystals 2.5 g./l.

Acetic acid—2 ml./1.

Triton X-100-0.2 g./l.

Duration overnight.

Fancy-16

# 2nd day: Dyeing:

Ursol A (BASF) : 3 g./l.

Ursol NZ (BASF) : 1.5 g./l.

Ursol EG (BASF) : 1 g./l.

Ursol Grey DM (BASF) : 1 g./l.

Liquor ammonia (sp. gr. 0.91) : 1 ml./l.

Hydrogen peroxide (20 volumes) : 15 ml./l.

Duration 1 hour.

Add to the same bath

Hydrogen peroxide (20 volumes) : 15 ml./l.

Duration 5 hours.

Wash the dyed skins thoroughly.

#### SCOURING:

 Syntan NC (CLRI)
 : 1 g./l.

 Triton X-100
 : 1 g./l.

Duration 30 minutes.

Wash well.

Allow to drain and apply the oil emulsions as described before under 'Dressing'. Hang to dry.

Drum the dried skins with saw dust for 1 hour or till the superfluous colouring matter is removed, cage, stake and grade the skins.

## Method 2:

(Hair treatment (Dyeing of tips/complete hair).

Prepare two solutions as follows:

## Solution 1:

Aniline oil : 36 g.

Add slowly, while stirring,

Hydrochloric acid (sp. gr. 1.2) : 54 ml. Water to : 500 ml.

-or-

Aniline hydrochloride : 50 g.
Water to make : 500 ml.

#### Solution 2:

Copper sulphate : 12 g.

Potassium chlorate : 15 g.

Ammonium chloride : 24 g.

Water : 500 ml.

Mix equal volumes of solutions 1 and 2 just before use. Apply the mixture on the hair, using a brush (for tip-dyeing use less). Leave the skins at 40°C for drying. Repeat brushing and drying twice or thrice more. (Mix the solutions afresh before each application). Wash thoroughly, dry and drum with saw dust etc., as for Method 1.

Note: Preparation of basic aluminium sulphate liquor.

Place 10 kg. of powdered aluminium sulphate (Al<sub>2</sub>(SO<sub>2</sub>)<sub>3</sub> 18 H<sub>2</sub>O) in a tub containing 10 litres of water. Stir well. Leave overnight for dissolution. Next day, add 700 g. of sodium citrate, dissolve by stirring; then add slowly, with constant stirring, soda ash solution (1.75 kg. soda ash in 20 litres of water). This liquor has a concentration of about 4% w/v. Al<sub>2</sub> O<sub>2</sub> and a basicity of 33%.

## K PARTHASARATHI & V. V. SUBRAMANIAM

Tanning hair-on and fur dressing have been a skilled art from prehistoric times. While fur coats were a necessity in ancient times, they have now become sophisticated appeal in the modern civilisation. Even forward trading is done in peltries. In India fur tanning and dressing have not yet registered any significant development, commensurate with the growth of the tanning industry. In India fur tanning is done on cottage and village level mainly in Kashmir, Himachal Pradesh and the neighbourhoods. The fur dressers in these areas follow the conventional alum tanning with the exception of a few who have the privilege of following scientific literature on the subject.

Almost every process on hair-on tanning aims at giving a soft leather without affecting the hair. Normally heavy hides intended for purposes other than fur coats are given direct chrome tanning while expensive fur skins are processed in many ways viz., simple pickle process, alum tanning, combination tannages and light chrome tanning. In all the cases, only the minimum quantity of the tanning material required to produce soft leather is given. In the case of chrome tanning only 1.5% chromium (Cr<sub>2</sub>O<sub>3</sub>) is given, giving a shrinkage temperature of about 80°C. In fur dressing, mechanical operations are of paramount importance and should receive much more attention than the tanning. The tanned leathers undergo a series of repeated operations like shearing, carding, staking in special machines and repeated dry drumming with saw dust of specified dimensions.

The tanning process given is adapted from the practice followed in some European fur dressing units and is mainly intented for tanning medium and light skins like tiger skin, yak skin, deer skin, wild cat skin, squirrel, rabbit skin, goat skin, etc. This has been repeatedly tried and standardised at the Institute and scaled up to a semi-commercial production level. The resulting leathers are extremely soft and maintain the original colour and texture of the fur/hair.

#### **PROCESS**

For wet salted and fresh (raw) skins, the skins are soaked for 4 hrs. with

500% water

0.1 % sodium trichlorophenate

0.1 % Triton X-100 (Rohm & Haas Co.)

0.5 % Zinc chloride (based on raw/wet salted weight)

For dried skins, 1000% water is to be taken and the rest of the wetting composition is the same as above. But the period of soaking is about a week, changing the soak bath daily with occasional beamings. It is very important to change the soak bath daily to preserve the hairs. Then the skins are pickled in the following way.

#### Pickling:

This is done with
Water—400%
Salt—40 g./l.
Zinc chloride 2 g./l.

Formaldehyde 2.5 g./l. } 1 hour

The percentage of water for pickling is calculated on the soaked weight of the skins and pickling is done in a pit or wooden tub for 4—6 days. The pH of the cut section of the skin is 2.5—2.8. Handling is done twice a day during pickling. After pickling the skins are beamed and taken for the next operation.

Prefatliquoring: Prefatliquoring is done with the following composition:

30 Sulfotan P (a solphonated mineral oil based Esso product)

1% Raw groundnut oil and

4% Water (50°C) (all based on soaked wt.)

The above mixture is made into a thick paste and applied on the flesh side of the pickled skins by hand and allowed to dry completely.

After drying, the skins are staked in the machine and shaved on the flesh side to uniform substance in the snaving machine. After shaving the skins are wetted back in 5% salt solution and chrome tanned.

#### Chrome tanning:

This is done with 100% water, and 1.5% Cr.O. (6% B & C chrome extract of 33½% basic).

The skins are run in the drum having 8 r.p.m. for about one hour After complete penetration, it is basified with 2% soda bicarb. Bicarbonate is given in four feeds at 10 minutes interval. Finally the drum is run for 45 minutes. The end pH is adjusted to 3.8-4.0. Then the skins are piled overnight. Next day, the skins are washed in plain water for 10 minutes in the drum.

#### Neutralisation:

This is done with 200% water and 1% soda bicarb, on soaked weight. The drum is run for 45 minutes. The bicarb is given in 3 feeds at 10 minutes intervals. pH of the cut section of the skin is 4.6—4.8. Then the skins are washed for 10 minutes in plain water.

# Refatliquoring:

This is done with 200% water (50°C)

4.5% Sulfotan P (Esso) and

1.5% Raw groundnut oil on soaked weight-

The drum is run for one hour. Then 0.5% to 1.0% formic/acetic acid is given in 3 feeds at 5 minutes intervals. After the acid addition, the drum is run for 20 minutes. Then the skins are piled overnight. Next day the skins are hung up for drying. After drying the skins are staked in the machine and dry drummed with saw dust moistened with mineral turpentine or trichloroethylene for 2 to 3 hours. After dry drumming the skins are aired off, trimmed and buffed on the flesh side with 150 emery paper. Then they are sprayed on the hair side with the following composition:

Formaldehyde 1 part
Formic acid 1 part
Ethyl/Methyl alcohol ½ part
Water 5 parts

After spraying with the above, allow the skins to dry for some time, then iron out on the hair side to produce lustre.

# S. L. SRIVATSAVA, I. M. S. PATEL & A. GANESAN

Kid skins of different colour having fine hair and curly wool are available in the northern region. Mostly these types of skins are collected from the pinjarapole sources. The skins having a peculiar type of curly design, in various colours possess a soft feel and beautiful appearance on finishing, particularly skins of still-born kids known as slunks are considered the best type. These varieties are sold in the Delhi market and the rate varies from Rs. 300/- to Rs. 500/- per score depending on their appearance. Most of these skins are exported to Western countries after preservation and are used after processing for fashion apparel wear, gloves, fancy goods, etc. These types of raw skins are available mostly in the states of Rajasthan, Gujarat and Madhya Pradesh.

At present, they are mostly processed after removing the hair like E.I. kid leathers, but they realise less value in the market as the cutting value is considerably less compared to E.I. goat and sheep. The wastage is thus comparatively higher to the shoe maker. Sometimes, the skins are dressed as fur by adopting conventional vegetable and/or alum tanning methods. By vegetable tanning, the skins acquire a reddish colour spoiling their natural appearance; they also lack softness. In the case of alum tanning, the skins are prone to weathering especially during the rainy season and lose their natural beauty. With a view to overcoming these difficulties, a process has been evolved, particularly to suit the cottage tanners in the Rajkot region, and is briefly outlined below:—

## Raw Materials

Wet salted kid skins of various colours and free from hair slip are selected for the process.

## Soaking

The skins are left in water for 1 hr. with 10% salt, then drained and washed in two changes of plain water taking 1 hr. for each wash. After proper soaking, the skins are removed, piled to drain off water

and the soaked weight is noted. It may be necessary to add the preservative to prevent hair slip on certain occasions.

# Pickling

The skins are pickled using 1% sulphuric acid, 0.5% formic acid and 8% salt on soaked weight. The acid is diluted and added in 3 or 4 instalments at 1 hour intervals. Next day, the excess flesh is removed by hand with the help of a rapi. After removing adhering flesh and keeping the skins in pickle for 10 days, 8% alum on soaked weight is added to the same liquor and the skins are turned over periodically and left overnight.

# Chrome Tanning

The pH of the pickle bath should be approximately 2.5. Half the quantity of the pickle liquor is removed and chrome tanning is commenced. Jaggery reduced chrome liquor equivalent to  $2\frac{1}{2}\%$  dichromate on soaked weight is taken. The chrome liquor is added in 4 instalments at intervals of 1 hour. The skins are handled in between for 15 minutes in the vat. After the final addition, the skins are again handled for 15 minutes, 0.5% cationic oil is added for more mellow feel and the skins are left properly immersed overnight. Two days later, they are basified with  $\frac{1}{2}\%$  sodium bicarbonate, dissolved in 10 times its weight of water and added in three instalments at intervals of 30 minutes and handling is continud. A boiling test is done. The tanned skins should withstand 2 minutes hot water at 86°C. The final pH should be 3.6-3.8. The skins are now taken out and piled flesh to flesh.

#### Neutralisation

Next day, the leathers are cleaned by shaving them lightly on flesh side in a well drained condition and weighed, washed in two changes of plain water, neutralised with 1% sodium bicarbonate on shaved weight (5% hypo gives better whitening effect) added in 4 instalments at intervals of 30 minutes. The pH of the cross-section should be 5.5-6.0. Again the skins are re-washed with 3 changes of plain water. The final washing is done in warm water at 45°C and the skins are then fatliquored.

# Fatliquoring

The skins are fatliquored with 4% TRO and 3% groundnut oil on cleaned weight. The oils should be mixed first and then dispersed in

water at 45°C. After fatliquoring, they are taken out and piled flesh to flesh. Next day, they are slicked and hung. Then they are dried, saw-dusted, staked by hand and hung up to dry completely. After drying, restaking on the edges, cleaning of flesh side and trimming an application of French chalk on flesh side is done.

The process is simple, easy to follow and does not involve the use of any machinery. The dressed skins are found to be quite good and the natural colour of the beautiful hair/curly woolies is retained. The skins have a soft feel and can be worked easily by the furrier. The skins are useful for making caps, children's shoes, chappals, straps and fancy articles such as toys etc.

# A RAPID PROCESS FOR ALUM OR VEGETABLE TANNING AND FINISHING OF REPTILE SKINS

#### R. SELVARANGAN & M. S. OLIVANNAN

Reptile skins like those of cobra, whip snake, Russel's viper, sand snake, python, lizard and crocodile are traditionally vegetable or alum tanned and exported from India without any finishing. The vegetable tanning is done mainly with avaram bark and is followed by myrobing and oiling. Alum tanning is done using potash alum or aluminium sulphate with addition of common salt and basification with soda ash almost up to precipitation point. The alum tanning is often followed by a treatment with formaldehyde and fatliquoring with a mixture of china clay, coconut oil and egg yolk. The salient features of the new processes presented herein are the quickness, simplicity and effectiveness of the tannage. The process has been simplified by using tannin extract or leach liquor in vegetable tanning and stabilised basic alum in alum tanning. Basic alum tanning is preferred for white tanning of reptile skins since it retains the colour and characteristics of the grain pattern of the raw skins. With a view to promoting exports of finished reptile skins, a general process for finishing of plain as well as coloured tanned reptile skins is also described.

#### TANNING OF REPTILE SKINS

Raw materials

Wet salted reptile skins are used.

## Soaking

The wet salted skins are soaked in plain water for 3 hours and given two changes of water. They are piled to drain and weighed.

# Liming

Liming is done with 10% slaked lime, 200% old lime liquor and 200% water. The skins are drawn one by one into the lime liquor and piled well inside the liquor. On the second day, they are handled thrice.

## Descaling and reliming

On the third day, the skins are descaled by trampling in a pit containing the minimum amount of water. After being washed they are relimed with 10% slaked lime and 400% water and are handled thrice. On the fourth day, they are handled thrice. On the fifth day, fleshing is done for all skins except pythons using a special fleshing knife. (The python skins are kept in the reliming bath for one more day).

# Deliming

The fleshed skins are washed twice and delimed fully with 1.5% boric acid and 150% water for two hours in a clean tub. The delimed skins are washed twice with plain water. The skins are now ready for tanning.

## Vegetable Tanning

Wattle tanning: The delimed skins are taken in a tub with sufficient water and the pH of the liquor is adjusted to 4.5 carefully by adding diluted formic acid in the course of 30 minutes. The skins are transferred to a tub containing 5°Bk wattle liquor prepared from spray dried wattle extract, handled twice in this bath and immersed well in the liquor very carefully. On the sixth day, the skins are handled thrice and strength of the liquor is brought back to 5°Bk. On the seventh and eighth days, the liquor is strengthened to 7°Bk and the skins are handled thrice daily. For the python skins, tanning in the 7°Bk liquor is continued for one more day.

During tanning, care must be taken to immerse the skins well in the liquor; otherwise the skins may start floating and produce stains. For this the float concentration may be maintained at 600% or above on the fleshed weight

# Bleaching and myrobing

On the ninth day, the tanned skins are removed and bleached with 1% Perfectan 'O' in a minimum volume of water. The skins are handled in this bath for 20 minutes and washed twice. The bleached skins are myrobed in 20°Bk myrobalan liquor, prepared the previous day from Salem myrobalan nuts. The skins are handled twice in the myrob bath on that day as well as on the next day (10th day).

## Oiling

In the evening of the 10th day, the skins are taken out, rinsed, wrung and oiled with 4% groundnut oil and hung on a string to dry.

# Drying and finishing

When leathers are in a sammed condition, they are pulled at both the edges. [Lizard skins are nailed on board and dried]. The dried skins are lightly ironed on the flesh side and are ready for export.

#### Alum Tanning

Upto deliming the procedure is the same as for the vegetable tanning.

## Pickling

The delimed skins are pickled overnight with 1% sulphuric acid, 5% salt and 150% water. They are handled repeatedly and left overnight in the pickle liquor.

On the sixth day, the skins are handled in the pickle bath for 15 minutes and then handled in a separate tub containing 14% aluminium sulphate liquor (66% basic), 0.5% chrome extract (B & C) and 150% water. The basic alum liquor is prepared using sodium citrate as masking agent. On the seventh day, the skins are handled thrice and the pH of the bath is raised to 4.2 using soda ash solution. On the 8th day, 2% formaldehyde is added to the same bath and the skins are handled well in the liquor. On the 9th day, the skins are handled and the pH of the bath is raised to 4.5 using soda ash solution. The skins are piled separately in the evening. For python skins, the tanning may be continued for one more day.

## Fatliquoring

On the 10th day, the skins are washed for 10 minutes and fatliquored as follows: The skins are first treated with 0.1% Tinopal BVN (a Geigy product) in 150% water at 55°C. The emulsified oil consisting of 2% Turkey Red oil and 1% raw coconut oil is added to this bath. The skins are handled for 30 minutes, rinsed and wrung.

# Drying and finishing

When the leathers are in sammed condition, they are pulled at both the edges. In the case of lizard skins, they are nailed on board and dried. The dried skins are lightly ironed on the flesh side which are then ready for export.

#### I. DRESSING AND FINISHING OF VEGETABLE TANNED SKINS

# (a) Brush dyeing and aniline finish (Golden brown colour)

The skins are lightly staked in a hand staker and buffed on the flesh side, if necessary. They are then pllain-plated in hydraulic press at low pressure (50 kg./sq.cm.).

Bottom coat: The skins are given one brush coat with 5% linseed mucilage solution and aired-off. The skins are then plated and a stain coat is applied.

Stain coat: Stain coat is prepared with 5 g. Metanil yellow (I.C.I.), 5 g. Naphthalene Orange (I.C.I.), 60 ml. 10% casein solution and water to make 1,000 ml. The skins are given a uniform brush coat and aired off.

Top coat: Top coat consists of 60 g. egg albumen, 60 ml. milk, 120 ml. 10% casein solution, 60 ml. formaldehyde and water to make 1,000 ml. The skins are given one pad coat, aired off, plated and then sprayed to cover. They are then glazed.

# (h) Finishing as coloured semi-alum tanned skins

The crust (vegetable tanned) skins are lightly staked and buffed, if necessary. The buffed skins are weighed and wetted back for 30 minutes in plain water. They are then given two changes of water and stripped with 1% borax and 400% water for 20 minutes. The stripped skins are washed twice and are bleached with 1% oxalic acid and 400% water for 20 minutes. The bleached skins are rinsed and retanned with alum.

The alum tanning is done with 7% aluminium sulphate (66% basic) in 400% water. The skins are handled in this bath for three hours and the bath is basified to a pH 4.5 using soda ash solution. The skins are handled for 1-1½ hours. The skins are then piled separately. Next day, the skins are washed for 10 minutes in 1000% water and then wrung. The skins are handled with 1% ammonia and 400% water at 55°C for 20 minutes. The bath is now drained and the skins are wrung. The skins are dyed with 1% Cibalan Blue

(Ciba, India) and 400% water at 55°C for one hour. Then to the dye bath itself, 0.5% Turkey Red oil is emulsified and added and the skins are handled for 20 minutes. Now 3% aluminium sulphate (66% basic) is added and the skins are handled for 40 minutes, then rinsed with water and squeezed. The squeezed skins are dried over a string and pulled at the edges. Next day, the skins are staked in a hand staker, plain plated in hydraulic press and ready for aniline finish. (All these weights are based on the crust weight).

# (i) Aniline finish

Bottom coat: 60 ml. 10% casein solution, 30 g. egg albumen and 100 ml. water. The plated skins are given one brush coat and aired off.

Top coat: 60 g. albumen, 100 ml. milk, 100 ml. 10% casein solution, 5 ml. nitrobenzene and 1000 ml. water. The skins are given one brush coat and aired off. Then a liberal coat is sprayed and the skins are aired off.

Fixing coat: The skins are sprayed with a fixing coat of 10% formaldehyde and aired off. The dried skins are glazed over a glazing machine.

# (ii) Glazing lacquer finish

The coloured skins are also aniline finished by spraying with 1 part CLRI glazing lacquer (clear) and 2 parts Spartan thinner (Addison Paints & Chemicals). The skins are sprayed liberally with this lacquer and aged for one day. Then they are glazed.

# (c) Finishing as coloured semi-chrome tanned skins

The process is the same as in semi-alum tanning upto bleahing. The bleached skins are chrome tanned with 4% chrome extract and 400% water for three hours. Then the pH of the bath is raised to 4.5 using soda ash solution in the course of 1½ hours. They are piled overnight separately. The rest of the treatments and finishing is similar as given under I (b).

# II. DRESSING AND FINISHING OF ALUM (WHITE) TANNED SKINS

# (a) Finishing as plain white

The white tanned skins are staked lightly and buffed on the flesh side, if necessary. Then the skins are plain plated at low

pressure in a hydraulic press and then sprayed with 1 part CLRI glazing lacquer (clear) and 2 parts Spartan thinner. The skins are sprayed liberally with this lacquer and aged overnight. Next day, the skins are glazed.

## (b) Finishing as coloured leathers

The crust leathers are staked lightly and buffed, if necessary and weighed. Then the leathers are soaked in 1000% water containing 1% Triton X-100 (Rohm & Hlaas product) for one hour. Then the skins are given two changes of water. Now the skins are dyed with 1% Cibalan Orange (Ciba India) and 400% water at 55°C for one hour in a tub. Then 0.5% Turkey Red oil is emulsified and added to the bath and the skins are handled for 20 minutes. 3% aluminium sulphate (66% basic) is then added and the skins are handled for 40 minutes. The leathers are rinsed and hung up for drying over a string.

The dried leathers are conditioned in moist saw dust and staked in a handstaker. Then they are finished either as aniline or with lacquer. The procedures are similar to the process described under I (a).

# PROCESSING AND FINISHING OF LITARD SKINS WITH GLAZING LACQUER

# V. RANGA RAO, A. DURAIKANNU, K. J. KEDLAYA, T. S. KRISHNAN & P. S. VENKATACHALAM

There is a demand in Western countries for lizard skins, processed and finished into leathers having good gloss with the finish film being water resistant. In India normally, lizards are vegetable tanned, retanned with chrome and protein finished. Such leathers have their own limitations. The tear strength is less and clear and bright pastel shades are not possible as the leathers are vegetable tanned. Hence processing of lizard skin by chrome tanning has been developed, as chrome tanned leathers can be finished into delicate fashion shades.

A salient feature of the chrome tanning process described herein is that the fatliquored and dried leather can be stored as crust; it can be wetted, dyed and finished as and when the order is received.

N. C. Lacquer, protein or alkyd compositions can be employed to finish the dyed lizards. Protein finish is not water resistant in nature. Alkyd finish is invariably tacky and possesses poor flexural endurance and requires a long drying period. N.C. Lacquer developed by CLRI not only helps in finishing lizards to a high gloss but also possesses the character of making the film water-resistant. The details of finishing of chrome-tanned lizards using N.C. glazing lacquer R.S. CLRI are given in the text. The procedure and the details of application of glazing lacquer R.S. given in this article are also applicable to the finishing of semi-chrome lizards.

As regards dyeing it may be noted that the leather could be dyed by "tie & dye" method if it is desired.

## Raw material:

Wet salted lizard skins assorted and weighed.

# Soaking:

(Percentages based on the raw weight) 500-600% water in wooden tub or pit. Handle for 15 minutes—Leave in bath for 1½ hrs.

Drain—give 2 or 3 changes of water—drain.

#### Liming:

300-400% water

3% sodium sulphide

Handle intermittently

Liming time—3 days

(Add the sulphide in 3 feeds, 1% each day)

On the fourth day, descale and flesh-Weigh

### Washing:

(Percentages based on the fleshed weight)

500% water

Duration—15 minutes

Repeat washing for another 10 minutes

## Deliming:

300% water

0.4—0.75% ammonium sulphate

Handle till the cross-section of the pelt is colourless to phenolphthalein (complete deliming)

# Bating:

300-400% water at 35°C

0.5% Oropon OR (Rohm & Haas)

Handling time 60-75 minutes

# Washing:

500% water

Handling time-10 minutes

# Bleaching: 1st bath

200% water

5% salt

0.5% potassium permanganate

(pH 8-8.5; Temp. 25-30°C)

Handling time—30 minutes

Drain

Fancy-18

2nd bath

250% water

8% salt

0.75-1% sodium bisulphite

0.25-0.5% oxalic acid

Handling time 45-60 minutes (till the brown colour due to permanganate has entirely disappeared).

If the skins are still not free from natural markings repeat the same procedure or bleach them further with sodium chlorite in pickle bath.

# Washing:

300% water

6% salt

Duration—10 minutes

Repeat the washing with salt solution for 10 minutes

Drain

# Pickling:

200% water

15% salt

0.5% formic acid (85%)

Handling time-30 minutes

Add 0.5-0.75% sulphuric acid (1.84 sp. gr.) + 10% water in 3 feeds at intervals of 30 minutes

Handling time—2.3 hrs. or preferably leave overnight after handling till the final pH is 2.8 to 3.

# Bleaching with chlorite:

Add 1-2% sodium chlorite (Hoechst) + 10-20% water in 2 or 3 feeds at intervals of 6 hrs.

Duration—2 days
Handle frequently

Add 2% sodium bisulphite+10% water to the same bath at the end of bleaching

Handling time 20-30 minutes

Drain

# Chrome tanning:

200% water

8% salt

Handling time—10 minutes

add chrome liquor (33\frac{1}{3}\% basic) containing 0.75\% Cr<sub>2</sub>O<sub>3</sub>

Handling time—30 minutes

Leave overnight

Next day add chrome liquor (33\frac{1}{3}\%) containing 0.75\% Cr<sub>2</sub>O<sub>3</sub> Duration—4 hrs.

Handle initially for 30 minutes and later handle intermittently

Add chrome liquor (33\frac{1}{3}\%) basic containing 0.75\% Cr. O. Handle for 30 minutes and leave overnight.

Handle intermittently

Next day check for penetration, pH and shrinkage temperature.

# Basification:

Sodium bicarbonate 1.00-1.25%

Water 20%

Add the bicarbonate solution in 4 feeds at intervals of 20 minutes Handle continuously. pH of bath is 3.7-3.8

 $T_a$  is > 100°C

Drain—pile for 24 hrs—sam—shave the neck and tail—weigh (All percentages calculated on shaved weight)

# Washing:

600% water

Handling time-20 minutes

# Retanning:

300% water

10% Tannigan 3 LN (Bayer)

Add Tannigan 3 LN (Bayer) which is dissolved in water in 3 feeds at intervals of 2 hrs.

Handle well after each addition.

Leave overnight

Next day handle intermittently and pile overnight.

#### Washing:

600% water

Handling time-20 minutes

### Neutralising:

300% water

Add 1.5-2% sodium acetate

+ 15-20% water in 2 or 3 feeds at intervals of 15 minutes

Handling time—45 minutes or more till the pH of the cut section is 5.0

Drain

## Washing:

600% water at 40°C Handling time—10 minutes

## Washing:

600% water at 50°C

Handling time-10 minutes

# Fatliquoring:

200% water at 50-55°C

Add 3% Sandozol KBS (Sandoz (India) Ltd.)

+ 1% Polyethylene glycol 600 (NOCIL)

+ hot water to emulsify (1:4)

Handling time 40 minutes

Check exhaust

If necessary, to exhaust, add 0.25-0.5% acetic acid + 5-10% water in 2-3 feeds at intervals of 5 minutes

Finally handle for 10-15 minutes

Check exhaust-drain-pile overnight

# Next day tack on boards to dry

When dry, remove, trim, buff on flesh with 240 grit paper and brush

Store the crust and finish as and when required.

#### Dyeing of crust:

(All formulations based on crust buffed weight)

#### Wetting back:

1000% water at 50°C

Add 3% Liquor ammonia (0.88)

0.5% Noigen LS (Chika Ltd.)

Handling duration—60 minutes

Leave overnight in the bath

Next day, handle for 15 minutes—check for proper wetting—drain

#### Washing:

1000% water

Handling time—15 minutes—drain

#### Stripping:

1000% water

50% salt

add 2-3% sulphuric acid

+ 20-30% water in 4 feeds at intervals of 30 minutes

Handle well after each addition

Duration-2-3 days

Handle intermittently

# Washing:

1000% water

30% salt

Handling time-10 minutes

Repeat washing for 10 minutes as above.

## Rewash:

1000% water

Handling time—10 minutes

Drain

# Rechroming:

500% water

Add chrome liquor (33½% basic) containing 1% Cr<sub>2</sub>O<sub>3</sub> Handling time—3 hrs.

Basify with sodium bicarbonate which is added slowly in several feeds and handle well till the pH of cross section is about 3.8. Drain—pile overnight.

### Washing:

1500% water

Handling time-15 minutes

Drain

### Neutralising:

600% water

Add 1.5-2% sodium acetate

+ 15-20% water in 2 or 3 feeds at intervals of 15 minutes

Handle till the pH of cross-section is more than 6.0 throughout—drain

#### Washing:

1500% water at 40°C

Handling time-10 minutes

Drain

# Dyeing:

1000% water at 50-55°C

Add 5% wattle extract powder dissolved in water (1:4)

Handle for 30-45 minutes—drain

1000% water at 50-55°C

Add 3% Derma Light Brown GRL (Sandoz)

+ hot water to dissolve (1:40) in 3 feeds at intervals of 10 minutes

Handling time-50-60 minutes

Add 1.5-2% acid formic (85%)

+ 15-20% water in 4 feeds at intervals of 5 minutes

Handle well after each addition and finally handle for 15-20 minutes

Check exhaust-drain

#### Wash:

1000% water

Handling time-5 minutes

Drain

Pile for a few hours—tack on boards to dry--Remove

#### Finishing:

1 part—N. C. Glazing lacquer RS (CLRI)

3 parts—Thinner (CLRI) or any proprietary (suitable) thinner

Spray 2 full cross coats

Dry overnight

Glaze under fairly good pressure

Spray again 1 wet cross coat—Dry well

Glaze again under light pressure.

#### Note

- (1) All the operations are done in wooden vats or tubs.
- (2) Where natural marking has to be preserved, bleaching operation is omitted and bating is done for a short duration with less bate or even omitted.
- (3) Descaling, if necessary, can be done by rubbing with coir rope or with brush.
- (4) Bleaching may be done after chrome tanning and shaving but bleaching prior to tanning gives better results.
- (5) Shaving may also be done after retaining with Tanigan 3 LN.
- (6) Stripping of chrome with sulphuric acid is, of course, not necessary where dyeing is done immediately after chrome tannage and neutralisation i.e. where the leathers are not crusted.
- (7) Suitable dyestuffs have to be used for getting the required shade.
- (8) The skins can be dyed by 'tie & dye' method if desired and finished.

The skins are initially dyed with a light colour after which they are tied for a specific pattern. They are redyed in a tub using a contrast dye, e.g.:

- (a) Base dye-3% Dermalight Brown GRL (Sandoz) Contrast dye-1.5% Atul Direct Black E Extra H/C (Atul).
- (b) Base dye—3% Dermalight Yellow GLN (Sandoz) Contrast dye—1.5% Sandopel Brown MS (Sandoz).

M. K. Roy & J. C. DEB

#### Introduction

Lizard skins have constituted one of the most important items of export from India for the last 50 years. Earlier the skins were exported in the raw condition, later they were exported in vegetable tanned crust condition. During 1968-69, the value of raw lizard skins exported was about Rs. 42.4 lakhs and that of tanned lizard skins Rs. 30.4 lakhs. With the development of tanning industry in India lizard skins are to some extent being converted to finished products and some finished skins have proved quite satisfactory to the foreign buyers. There is much scope for exporting finished skins especially to U.S.A., Italy and Japan. Hence we should rather direct our efforts to exporting lizard skins in the finished condition in order to earn more foreign exchange. With this end in view, some processes have been developed and are described here.

#### (I) MANUFACTURE OF PICKLED LIZARD SKINS

#### Raw material

Wet salted lizard skins of good quality. The raw stock is weighed.

### Soaking

The skins are washed in plain water in a pit. They are then soaked in a pit in the evening and left overnight. The soaking bath is prepared using 0.25% sodium sulphide and 200-300% water (on raw weight).

# 1st Liming (in pit)

Sodium sulphide 2% (on raw wt.)
Lime 1% ,,
Water 100-150% ,,

The skins are put in the lime bath prepared as above. They are handled in the bath for 30 minutes in the morning and 30 minutes in the evening and kept in the lime bath for 2 days.

2nd Liming: The skins are then put in second lime liquor prepared with 7.5% lime and 300% water. They are kept in the bath for 3-4 days and handled twice daily until descaling is complete.

# Washing and Deliming

Washing is done thoroughly in two to three changes of water in a pit until the scales are completely removed.

The descaled skins are delimed with

Ammonium sulphate	0.75%	on	limed	weight
Water	200%			

in a drum by running it for 30-45 minutes until deliming is complete. The bath is then drained out and the skins are washed thoroughly in plain water for 30 minutes. The bath is then drained.

### Bleaching

Bleaching bath is prepared in a drum as follows:

Potassium permanganate	0.1%	on pelt wt.
Sulphuric acid	0.2%	,,
Watèr	100%	,,

The goods are run for 20 minutes and the bath is drained.

Then the skins are run again in a drum containing

Sodium bisulphite	5%	on pelf wt.
Oxalic acid	0.25%	,,
Water	100%	,

for 30 minutes and drained. The goods are now ready for the next operation.

Note: The procedure may be repeated to get the desired depth of bleaching effect.

#### Pickling

The skins are then pickled in a drum with:

Salt	10%	on pelt wt.
Water	80%	,,
Oxalic acid	0.25%	,,
Preventol	0.05%	

The drum is run for 30 minutes.

0.25% Formic acid is then added and run for 30 minutes followed by 1.25% sulphuric acid (diluted in ten times water)—added in three equal instalments at intervals of 30 minutes. After the last addition the goods are run for one hour and left overnight.

Next day the goods are run for one hour more and the pH is adjusted to about 2-2.5.

#### Preservative treatment:

Half of the pickle liquor is then drained out and 20% salt and 0.25% Preventol or any other suitable preservative are added to the same pickle bath and the drum is run for 30 minutes. The goods are then drained and packed in polythene bags and put into the covered wooden cases for export.

#### (II) MANUFACTURE OF VEGETABLE TANNED CRUST LIZARD SKINS

Upto deliming and washing the process followed is the same as stated under process (i).

### Pickling

The pickle bath is prepared in a drum with 6% salt and 75% water (on limed weight). The drum is run for 10 minutes and 1.25% sulphuric acid (on pelt weight) diluted in water is then added in three equal instalments and run for one hour after the last addition. The final pH is kept around 3.5.

#### Pre-treatment

The skins are taken in a wooden tub along with CLRI Syntan PC 2% and water 10% (on pelt weight). Handling is done for 1 hour. The skins are then kept overnight in the bath.

#### Vegetable tanning

Then another liquor is prepared in a pit as follows:

Sonari Bark

100%

Salem myrobalans (Crushed)

10%

Water

300-400%

(preferably water at 60-70°C).

10% G. S. Wattle powder is dissolved separately in 50% water in a wooden vat.

The tanning is started in pits with 5°BK liquor prepared from the soaked bark mixture. The skins are kept in the liquor for 2-3 days with hauling and replacing at least twice a day.

The liquor strength is then raised to 7-8°BK with the stock liquor and the skins are kept in this liquor for 2-3 days with hauling and replacing twice a day.

In this way the liquor concentration is raised upto 15-18°BK and the skins are handled as stated above. The stock liquor prepared from G.S. Powder is used to prepare liquor of higher concentrations starting from 10°BK. The total time required for tanning is 8 days. The tan liquor penetration is checked and the skins are they taken out. The skins are then piled overnight covering them with gunny or polythene paper.

# Washing and Bleaching

Next morning the skins are washed in pits with two changes of water each for 30 minutes. The skins are then bleached in pit or preferably in wooden vat with the following chemicals:

Sodium bisulphite

1 part

Water

12 parts

They are handled for 10 minutes and then 2 parts of oxalic acid are added.

The skins are then handled further for 30 minutes. The bleaching bath is then drained out. Washing is then done in 2 changes of water.

### Myrobing

A stock myrob liquor is prepared in a pit with:

Crushed myrobalan

10% on pelt wt.

Water

40%

Myrobing is done with a liquor of 10°BK prepared by diluting the stock liquor. The skins are handled in this liquor for 30 minutes and then left overnight in the bath.

# Oiling

Next morning the skins are taken out and oiled with groundnut oil. They are then hung up for drying.

# Staking

On the following day they are staked in hand staker.

# (III) MANUFACTURE OF VEGETABLE TANNED AND FINISHED LIZARD SKINS

Upto tanning the process is same as stated under process (ii). The skins are then taken for further processing.

# Stripping

This is done in a drum with:

Soda ash Water  $\left. \begin{array}{c} 0.5\% \\ 1500\% \end{array} \right\}$  on tanned weight

The drum is run for 30 minutes. The bath is then drained out and the skins are washed in the drum for 30 minutes.

### Retanning

The following recipe is followed for retanning in a drum:

B & C Chrome powder

 $\left.\frac{4\%}{500\%}\right\}$  on tanned weight

The drum is run for 45 minutes. The bath is drained out and the skins are washed for 30 minutes.

# Dyeing and Fatliquoring

A dye solution is prepared with the following dyestuffs:

Nigrosine G 140 (ICI Ltd.) 0.2% Chlorazol Black (-do-) 0.2% Naphthalene Leather Black 12 BS (-do-) 0.2% The skins are taken in a drum along with 100% water on tanned weight. The dye solution is then added and the drum run for 45 minutes. 0.2% Formic acid (on tanned weight) diluted with water is then added and drumming is continued for 30 minutes.

In the same bath the following fat mixture emulsified with hot water is added.

T.R.O.	1%
Sulphotan P (ESSO)	1% on tanned weight
Dermolin (Blue Bird)	1% ∫

The drum is run for 45 minutes. 0.2% Formic acid is then added to exhaust the fat liquor if necessary. The skins are then taken out and piled overnight. Next morning they are hung up for drying

On the following morning the skins are staked in the hand staker. They are then ready for finishing.

### Finishing

Bottom season is prepared as follows:

Hematin	1.5 parts
Naphthalene Leather Black 12 BS	1.5 ,,
Nigrosine G 140	1:5
10% Casein solution	5 "
Egg Albumin	5 ,,
Neran Glaze Finish (ICI)	5 · , ,,
Diethylene Glycol or other plasticiser	1 part
Green dye	0.1
Black pigment	0.2 ,,
Formalin	1 ,,
Preservative as required, water to make	200 parts.

Two brush coats are applied with subsequent hand staking and glazing.

The top season is then prepared as follows:

Bottom season	1 part
Neran Glaze Finish	1 ,,
Formalin	1,
Water	2 parts

Apply one brush coat and then glaze.

#### MANUFACTURE OF TURTLE LEATHERS

#### B. DURAISWAMY & T. J. DEVASSY.

Turtle leathers which are very similar to crocodile leathers in both look and pattern are nowadays used for making fashion articles like ladies' hand bags, wallets, purses, ladies' shoes etc. As only flippers are used for leather making, the effective area obtained is very small. Leathers and leather goods are made in Europe and America out of raw turtle flippers imported from Africa and South American countries.

Turtles are caught mainly for food. Green turtle (chelonia mydas) is the species most sought for. Hawks Bill turtle is valued for its shell and used for soups and steaks. Logger head turtles have very little commercial value.

In India, turtle is available in the eastern coast of Pamban in the gulf of Mannar, the Sundarban areas in West Bengal and the Ganges in U.P. It is estimated that about 5000 turtles are caught annually in Madras State alone. A process is described here to utilise the available turtle flippers and make leathers of good export value.

#### Raw Material

Turtle flippers in dry salted condition were used as raw material.

### Soaking

The flippers were soaked in water containing 0.3% sodium trichlorophenate and 0.75 to 1% Triton-X 100 on the volume of water which may vary between 300 to 350%. After one day's soaking, the skins were given a beaming on the flesh side to facilitate quicker soaking. The pieces were left again in the same bath for one or two days more, to effect complete soaking. When soaked completely they were given two to three changes of water and allowed to drain.

# Liming

The pieces were limed with  $1\frac{1}{2}\%$  sodium sulphide, 5% lime and 300% water. They were handled in this lime and sulphide bath for two days and on the third day the scales on the grain side were

removed by using an unhairing knife in the usual manner. Special care must be taken to avoid scratches and knife marks on the grain.

#### Reliming

The descaled pieces were then relimed with 5% lime and 300% fresh water and were handled in this bath for 5 days, handling being done twice a day.

### Fleshing & deliming.

The relimed pieces were hand-fleshed very carefully avoiding flesh cuts and the small bones were removed without creating any slits. As the pieces were small in size, maximum care was taken at this stage to prevent the wastage of pelt area.

The fleshed pieces were weighed (pelt weight), washed in plain water for 20 minutes in drum and then delimed with 1½% ammonium chloride and 200% water for 2 to 2½ hours the completion of deliming being tested with phenolphthalein.

#### Pickling

The delimed pieces were washed once with water and then pickled with  $1\frac{1}{2}\%$  hydrochloric acid of specific gravity 1.18, 10% salt and 100% water (on pelt wt.) for  $2\frac{1}{2}$  to 3 hours. The acid was diluted and then fed in two instalments at 15 minutes interval. After the second addition, the drum was run for 2 hours and the goods were left overnight. The end pH was about 2. Instead of hydrochloric acid, sulphuric acid also can be used.

### Chrome tanning

For tanning, chrome liquor corresponding to 5% dichromate on the fleshed weight of the pieces was used. The chrome liquor was added to the pickle bath in three instalments. After the addition of the 1st instalment, the drum was run for 1 hour and the remaining two instalments were added at thirty minutes interval and the bath was then basified with \frac{3}{4} to 1% sodium bicarbonate to get an end pH of 3.8. The skins were run in the basified bath for one to one and half hours more to complete the chrome tanning and the leathers were then aged for two days.

## Sammying & shaving

The aged leathers were sammed by machine and shaved on the flesh side for uniform substance, weighed and taken for bleaching.

#### Bleaching

The shaved skins were washed in water for 10 minutes and then bleached in a separate bath using potassium permanganate, sodium bisulphite, common salt and oxalic acid. The skins were first drummed in 1% solution of potassium permanganate for about 45 minutes after which the pieces were removed from the drum and allowed to drain completely. Separate reduction bath was prepared in the drum using 4 kg. of sodium bisulphite and 4 kg. of salt for every 100 kg. of float used for the process. The pieces were run in this bath for ten minutes and then  $\frac{3}{4}$ —1 kg. of oxalic acid (for every 100 kg. of water as given above) was added to the drum in two instalments at ten minutes interval. The drum was finally run for 40 minutes and then leathers were checked for satisfactory bleaching. If necessary, bleaching may be repeated to obtain very good results. Permanganate bleaching can be done just after deliming also.

#### Neutralisation

The bleached pieces were washed with water for ten minutes and then neutralised with 1 to 1.5% sodium bicarbonate and 150% water for 2 hours, washed with water and taken for fatliquoring.

# Fatliquoring & retanning

The pieces were fatliquored with 100% water at 55°C and 8% fatliquor using Lipoderm Liquor II (BASF) and raw neatsfoot oil in the ratio 3:1. The drum was run for 30 to 40 minutes and to the same bath was added 5% cutch extract. The drum was run for another 45 minutes to exhaust the bath completely. The pieces were then removed and piled overnight.

### Setting & drying

On the next day the skins were set out on the flesh side and hooked up for complete drying.

### Saw-dusting & staking

The well dried skins were saw-dusted overnight, staked lightly, preferably by hand and then nailed on boards without giving much stretch and allowed to dry.

#### Buffing & finishing

The dried pieces were buffed on the flesh side to obtain a smooth surface and the grain finished in suitable colours. For instance, the pieces were first stained with 2% solution of the required dye and allowed to dry well. One more coar of the stain was applied to get good cowering. Then a pigment composition as given below which will give contrast effect to the base colour was applied.

Water	3: parti
Resin Binder IM (Chika P. Ltd.)	1 part
10% Casein dispersion.	1/5 part
Hilco Pigment	1. part

The season was sprayed at an angle to give two tonic effects and for this the leathers were well fixed on spring boards on all four sides; when dried completely the pieces were sprayed with CLRI lacquer diluting the same in the ratio 1:2. Alternately, solvent soluble dyestust solutions mixed with lacquer can be sprayed to obtain beautiful aniline and two-tone effects.

# M. B. CHAUHAN, L. M. PRASAD, I. M. S. PATEL & T. J. DEVASSY

Though shark skins are generally sold along with the meat in the Saurashtra region, it is possible to get a fairly good supply of shark skins owing to the pioneering efforts of the Central Institute of Fisheries Technology A process for producing shrunken grain shark skin leathers is presented in this paper inclusive of a detailed study of the several variations tried before the process was finally streamlined. In processing shark skins, no attempt has been made to remove the scales which are really responsible for imparting the characteristic appearance of shark leathers. The shrunken pattern is also distinct for shark skins as it is longitudinal in design.

India with an extensive coastline has a good potential for supply of shark skins. Recently, an attempt has been made to use the skins of shark for leather-making on a large scale. The main difficulty has all along been non-availability of skins as normally the skins are sold along with the meat. As a result of development of the fish meat processing industry, the establishment of shark liver oil factories and the interest and efforts taken by the Central Institute of Fisheries Technology, it has now become possible to get a fairly good supply of shark skins in the Saurashtra region. The Institute has developed a method for easy skinning of the fish without damaging the skin.1 The estimated total production of shark skins in the country is about 2 million sq.ft., if properly utilised. There is a wide variety of sharks, their sizes varying from 1 to 8 ft. in length; sharks measuring 3 ft. and over are available only in small numbers. The best type of skins for the footwear industry falls within the range 25 to 36 inches in length. Skins of smaller size have poor cutting value.

As shark skins have a lower Shrinkage Temperature as compared to mammalian skins, it is necessary to store the cured skins in a cool place. Two natural properties of these skins are taken advantage of in the process developed. No attempt has been made to remove the scale on the grain surface which is very fine in the case of small skins and comparatively coarser in bigger skins. By retainning the scales, it is possible to impart a special look to these skins and their natural sheen can also be maintained in the finished leathers. Secondly, the grain is very loosely connected with the lower layers of fibrous matter. There is a natural formation of

wrinkles which can be made flat by mechanical operations like striking out and setting out especially after vegetable tannage to yield a very smooth grain. It was therefore thought better to shrink the grain in a suitable manner to produce a uniformly shrunken appearance. The shrinkage takes place only longitudinally, thereby imparting a characteristic appearance, which cannot be obtained in any other type of leather.

A process developed for the production of shrunken grain leathers from shark skins is described below:

The skins cured with common salt and stored for one month are soaked for a few hours in water, worked over a beam on the flesh side, washed and taken for liming. The lime liquor is made up of 10% slaked lime and 300% water on the soaked weight, together with a small quantity of old lime liquor. After 3 days, handling being done once daily, the skins are worked on the beam and relimed. with 10% slaked lime on the 4th day. Care is taken not to damage the grain side. On the 8th day, the skins are fleshed, washed, delimed with 1% ammonium sulphate beamed again, washed, drained and taken for the shrinking operation. The materials used for this are 15% myrobalan powder, 5% myrobalan or wattle extract and 1.25% formic acid (on the pelt weight). The goods are smeared with myrobalan powder and then drummed for a few minutes. Formic acid and extract mixture are then added to the drum in two instalments; the drum is run for 3 hours and rested overnight. Next day, the goods are drummed for 30 minutes, taken out and washed for 15 minutes in water. Special care has to be taken to avoid evolution of heat during drumming. This is followed by chrome tanning which is done in the usual way, using 4% dichromate equivalent of basic chromium sulphate (on the pelt weight) fed in 3 instalments. The final pH is adjusted to about 4 after which the goods are removed, sammed and shaved to proper thickness. The skins are washed thrice in plain water and neutralised using 1% sodium sulphite on the shaved weight (1/3rd from grain and 1/3rd from flesh). After a further washing, they are fatliquored with about 7% fatliquor using equal amounts of T.R.O. and groundnut oil at a temperature of about 40°C. It is better to avoid fish oil which imparts a bad smell. to the leather. The goods are then piled, slickered on flesh side and dried. When dry, the leathers are conditioned in moist sawdust, staked by hand and fluffed.

The grain pattern formed depends to some extent on the type of shark skin, but in all types, attractive patterns are obtained. The

finishing has to be so adjusted that the natural scales are not covered with pigments. An initial dye application is given by brush and then a combined dye-pigment coat is given, keeping the pigment content low. Such a composition is found to enhance the natural lustrous appearance. As a binder, CLRI Acryl binder MS (or any proprietary resin binder) is used. In order to obtain good gloss and enhanced sheen, one or two coats of top gloss (Imidol or CLRI top gloss) mixed with dye are given. The leathers are found to be pliable, strong and quite attractive with a characteristic look of their own.

The process has to be modified suitably depending on the condition of the raw stock. When the skins are not fresh, and not properly stored, the leather prepared by this process will get completely split up into layers thereby making it very weak. Further, due to the presence of vegetable tanning material, the natural sheen is found to be lost to some extent. Hence, the following changes should be made. Liming is shortened by 2 days and for shrinking, the goods are first treated with 2% formaldehyde for ½ hour and then chrome tanned as usual along with 3% salt after adjusting the initial pH to about 3.0 with formic acid. Skins thus processed are found to retain their strength and natural sheen.

The leathers can be used for making gents' shoes, ladies' handbag and shoes, fancy articles, purses etc. As shoe upper, the leather possesses all the required physical characteristics. (Table I)

TABLE 1

Sample		Tensile strength (psi)	% Elongation	Stiteh tear (lb/inch)	Tongue tear (lb/inch)	Bursting strength (lb/inch);
•	<del></del> :		<del> </del>			
Shrunken-	=	3764. <b>2</b>	59	574.8	334.2)	
grain	Τ.	1 <b>737.4</b>	41	479.1	323.2	7,874
Shrunken-	= . •	3025.2	53	<b>552</b> :5	495.3)	
grain	Ţ,	2707.4	53	531.1	311.7	10,294
Chrome-		1719.1	40	698.5	492.1	
tanned	1	2489.5	61	746.1	<b>55</b> 5.6 }	11,723

A few dozens of shoes have been made using vegetable tanned and shrunken grain shark leathers. The shoes have turned but quite attractive in appearance and proved comfortable in wearing trials. The shoes are being tested further for wearing qualities.

### Effect of different types of liming

It has been found necessary to find out the best system of liming as related to the strength of leather, its softness and the intensity and uniformity of pattern formed during shrinking. The following liming systems have been tried:

- 1. 0.5% caustic soda. + 10% lime
- 2. 1% soda ash + 10% lime
- 3. 1% sodium sulphide + 10% lime
- 4. Old lime liquor + 10% lime
- 5. 10% new lime only
- 6. Same as 4 & 5, but longer duration

[All percentages are based on the soaked and drained weight of the skins]

After liming for 5 days, the above pieces were tanned as per the process already outlined. It was found that system no. 5 produced the strongest leather and no. 4 reasonably strong leather. But in the other cases, the strength was very much reduced, even leading to structural breakdown. In such cases the shrinkage also was not uniform as the structure was already affected by swelling. Though both no. 4 and no. 5 produced well-shrunk leathers, no. 4 yielded leathers that were softer. When in systems no. 4 and no. 5, the period of liming was increased to 10 days, it was found that the strength was reduced considerably. But the pattern produced in shrinking was better than that obtained after short liming. In this case also, the strength was much reduced, when the period of liming was beyond 10 days. Considerable work is therefore necessary to find out exactly how the structural breakdown occurs in such cases. It can be stated that drastic treatment during liming has to be avoided and optimum period of liming must be given to obtain the best feel, strength and pattern. It can be also stated that if the skins are fresh, the deterioration in strength due to liming treatment is correspondingly less.

### Effect of pretreatments on leather

As different pretreatments will have their own effects on the final leather, an attempt was made to find the right type of treatment in order to obtain the most satisfactory type of leather. The period of liming and other details followed were the same as in the standard process described earlier. The effects of the following, before chrome tanning, were studied.

1. Vegetable tanning : 25% aval bark

2. 2% formaldehyde

3. 3% CLRI Syntan (pretreatment type)

4. Pickling : 2% hydrochloric acid & 10% salt

5. Bating : Bate leathcol 2%

[The percentages are based on pelt weight]

By pretreatment with vegetable tanning material (aval bark), the grain did not shrink properly, the strength got reduced and the final leather when finished was not bright. On the other hand, formaldehyde treatment makes the leather very soft, with a reasonably good shrunken grain (though not very uniform). The strength is also considerably higher and the leather lends itself to finishing very well. In the case of leathers tanned after a syntan treatment, the feel is reasonably good, but the pattern is not satisfactory and the strength also gets very much reduced. When pickling is done before tannage, the resultant leather is found to have a reasonably good feel, with a slightly reduced strength and the final leather has a very good finished appearance. It was found that during bating, the pelt pieces got crumpled because of the high temperature. Hence it has been found that a mild pickling combined with formaldehyde treatment before further processing will be very beneficial in producing satisfactory leathers.

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#### P. S. VENKATACHALAM, K. M. PARTHASARATHY & Y. NAYUDAMMA

The larger variety of Indian frogs (Rana tigrina) from Malabar are edible and their legs are processed and exported. It was thought that the skins of these frogs which do not at present find any other use may prove to be of commercial value if tanned and finished. Exploratory work was therefore undertaken to find out how best these raw materials could be processed to achieve maximum economic utilisation.

Only flint dry frog skins were available for the initial experiments. These skins are smaller in size and lack the beautiful design found on those obtained from East Asian countries. Soaking, liming and bating had necessarily to be carried out for a prolonged period to achieve the desired degree of mellowness in the final leather, even though they had an unfavourable effect on the clarity of the markings. The latter are important and should be preserved if the frog skins are to have eye-appeal. The introduction and promotion of their use in the leather goods industry may depend on how well the markings are preserved and their appearance enhanced by judicious processing and finishing by the dresser. It was pointed out to the supplier that it is from this aspect only that they should be preserved by wet-salting. Subsequent work showed that wet-salted skins gave leather with more prominent markings, mellower handle and greater area-yield.

From the point of view of markings, the skins could be graded into 3 groups, viz., (i) those that have a spotted leopard like appearance, (ii) the ones that have strong protuberant markings running from head to tail and (iii) skins which show comparatively weaker markings. In using the leathers for making goods, it is advisable to use the last-mentioned variety for gussets and other components which will not be in prominent view.

The initial experiments were entirely devoted to making white leathers in order to bring the markings into bold relief. Tanning with basic aluminium sulphate, alum and formaldehyde, self-tanning with Supra type syntan, combination of chrome and Supra syntan,

zirconium tanning, direct tanning with basic aluminium sulphate without liming were all tried without success. Direct tanning after soaking produced excellent markings, but the leather was distinctly tinny and cracky. The other tannages yielded products that had rather poor markings and were inclined to be somewhat empty. To sum up, these leathers were definitely unsaleable:

The above line of work was abandoned. However, vegetable tanning was found to produce a softer leather with poorer markings. When followed by pigment finishing, the markings were found to be obliterated. It was thought that an 'aniline' type of leather, glossy, bright and mellow displaying at the same time the markings in reasonable contrast, should be the ideal type of product that can be processed out of frog skins.

After a number of experiments, a process was arrived at whose salient features are outlined here:

- 0. Weigh goods (Raw weight).
- 1. Soaking: flints in 1000% water and 0.2% Preventol liquid I (Farben Fabriken Bayer) ... 2 days wet-salted skins in 400% water ... 2 hours
  - 2. Washing: thrice in 500% water
    Drain and weigh (soaked weight)
  - 3. Liming: 400% old lime liquor, free from sludge; 1-2% slaked lime ... 4 days

    Handle mornings and evenings and scrape flesh with a blunt pen-knife
  - 4. Reliming: 300% water and 1-2% slaked lime ... 2 days Handle and flesh as under 3. Weigh (pelt weight).
  - 5. Washing: overnight in 400% plain water.
  - 6. Deliming: 0.5% NH, Cl and 200% water ... 1 hour
  - 7. Bating: 0.5% Bate (Pancreol 3 AS) and 200% water at 40°C ... 2 hours
  - 8. Pickling: 200% water, 12% salt and 2% HCl... 1 hour Leave overnight.
- 9. Depickling: 200% water and 6% Hypo ... 24 hours

- 10. Tanning (vegetable): rinse and tan with avaram bark as for E.I. skins ... 7 days
- 11. Myrob bath ... 1-2 hours
- 12. Drain, samm, oil up and hook to dry.
- 13. When dry, weigh and wet back.
- 14. Retan with 4-6% Tanigan Supra LH (Farben Fabriken Bayer) and 300% water .... 24. hours

The retained leather is rinsed and dyed with 0.11-0.2% (on crust weight) amphateric dyes or basic dyes that are reasonably light-fast, fattiquored with 11-2% sulphated coconut oil, piled overnight, lightly struck out-and maked to dry.

When dry, they are removed from boards, trimmed, buffed seasoned with a mixture of milk and egg-albumin and glazed under light pressure. Leathers so finished turn out quite attractive in appearance, and have been made into hand bags, wallets, pouches etc. They are found to have retained their flexibility and strength after storage for 3, years.

#### P. S. VENKATACHALAM & K. M. PARTHASARATHY

The bandicoot rat is probably the biggest species among the rat family. Some of the Latin names in use to describe this specimen are Mus malabaricus, Mus giganteus, Nesocia bandicota and Bandicota Bengalensis. Bandicota Bengalensis is, however, much smaller in size. It is also known as the Malabar rat or pig-rat, the latter name being descriptive of its size which is similar to that of a small pig. Actually, the name bandicoot is a corruptive form of the Telugu word Pandikokku which literally means pig-rat.

The animal is known to inhabit all parts of India particularly the cities and towns. In fact, the bandicoot follows an urbanwards migration pattern that is similar to that of the human beings. It is probably because food and refuse are easier to come by in human habitats than in the open fields except probably during the harvest periods. Though the bandicoots are omnivorous, they appear to have a partiality for grain and roots and as such are very destructive in fields and gardens. They are a menace to residential areas also and dig into masonry walls with ease cutting labyrinthine holes underneath dwellings, probably causing a weakening of their very foundation. will thus indirectly contribute to Destroying bandicoot rats better conservation of food and protection of crops, apart from its hygienic significance. The skins of bandicoot rats have promising leather making potential as will be evident from some of the preliminary tanning trials conducted in the Central Leather Research Institute. Madras.

About 500 skins were purchased locally and tanned E.I. fashion. The process is exactly the same as for frog skins (vide pages 159-161).

Some of the crust leathers were retanned with chrome and finished into semi-aniline leather. A few of the finished leathers were hair-cell plated. They were found to possess a sheepy character with a tight grain. The pieces can readily substitute sheep skins for lining purposes. Sandal straps can be conveniently cut from them and used to supplement our upper leather resources.

The most important part of the bandicoot skin is however its tail. The tail is scaly and is about two inches wide at the top and tapers towards the end. It is approximately 8-12" long. The scales leave a fine lattice pattern which is characteristic of the bandicoot. As such, the tails are ideal for making watch straps. As the tails are tough they have good abrasion resistance and do not form ugly permanent creases even after repeated flexing. The lustre on the finished strap can be readily developed or restored by simply polishing it with a brush or rough cloth in view of its good surface-hardness. There appears to be good potential for utilising the skins for gas meter diaphragms as they have a sheepy texture, reasonable strength and the required thickness for such purposes. Care should, however, be exercised in selecting the crust leathers as bandicoot skins appear to be more susceptible to defects than other types in view of their predatory habits.

#### K. RADHAKRISHNAN

Leather board is a kind of fibre board which contains mostly tanned collagen or leather fibres. Leather boards are used in the footwear industry, as insoles, stiffeners, mid-soles, heel lifts etc. and also in leather goods industry for making certain articles or as lining. They are made from tannery waste materials like leather trimmings and shavings. Leather boards are manufactured in India to a limited extent. A process for the manufacture of leather boards for use as insoles, is given below:

The leather trimmings are shredded into fibres in dry condition in a rotary cutter. The resulting fibres are then wet ground in toothed disc mills or Hollander type of Beater. The length of fibre is an important consideration in the manufacture of leather boards. Fibres should not be too long or too short. The pulp is washed and well beaten in the Hollander with the addition of the following reagents - a wetting agent, a little dye, sulphated oil and the binder which in this case is 60% rubber latex. The amount of binder depends on the end use of the board. For an insole leather board, normally 25 to 30% latex (on the weight of dry leather fibres) is added. The slurry is kept under agitation in the mixer and the latex is precipitated around the leather with 5% aluminium sulphate solution, which is the coagulating agent used. pH of the pulp is tested periodically and when it is 4.0, addition of alum is stopped. A little preservative is added at the end. Now the process is complete.

# Board making

Measured quantities of the pulp are let into suction boxes for filtration. Filtration is hastened by applying vacuum. The well adhered wet sheets are stacked in a hydraulic press and pressed slowly to remove as much of water as possible. The boards are dried in shade and when they are dry, they are calendered to smoothen the surface in a calendering machine. The edges are trimmed and the boards are now ready for despatch or storage. The thickness of boards can vary from 1 mm. to 3.5 mm. depending upon the use. The normal size is 3' × 2'.

The physical properties such as tensile strength, stitch tear strength, flexibility etc., are tested to conform to standards.